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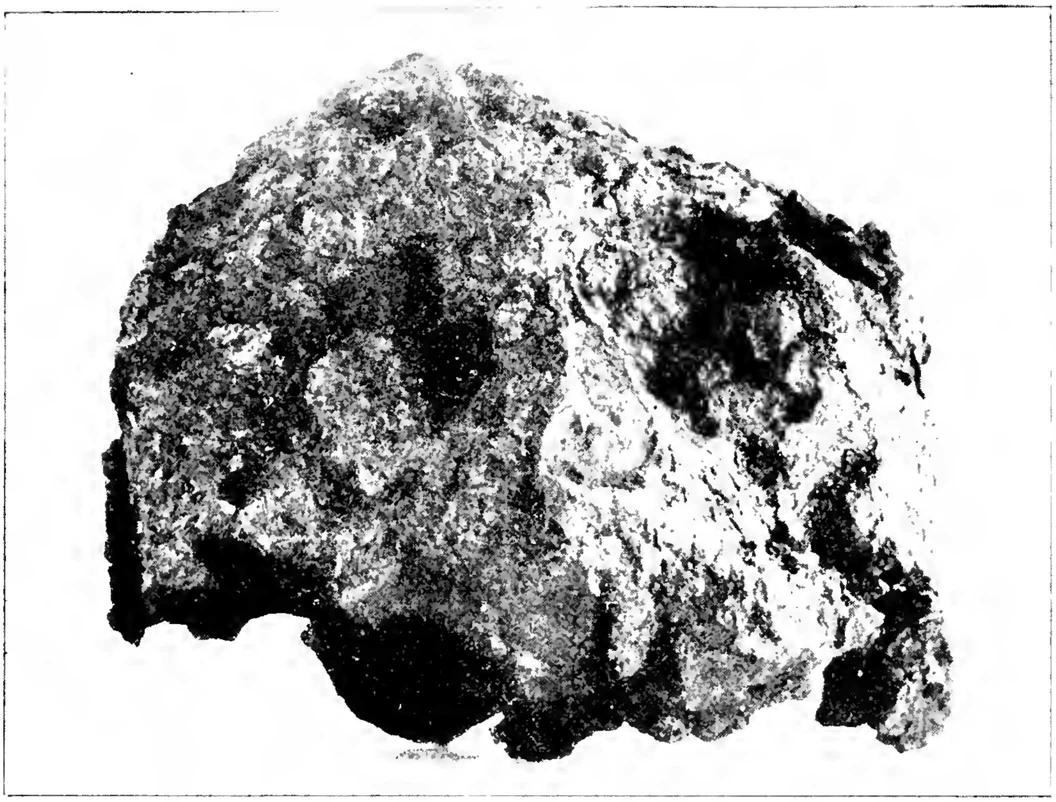

FIG. 1. — PREHISTORIC PALLASITE BEFORE CUTTING.
[Closely natural size.]

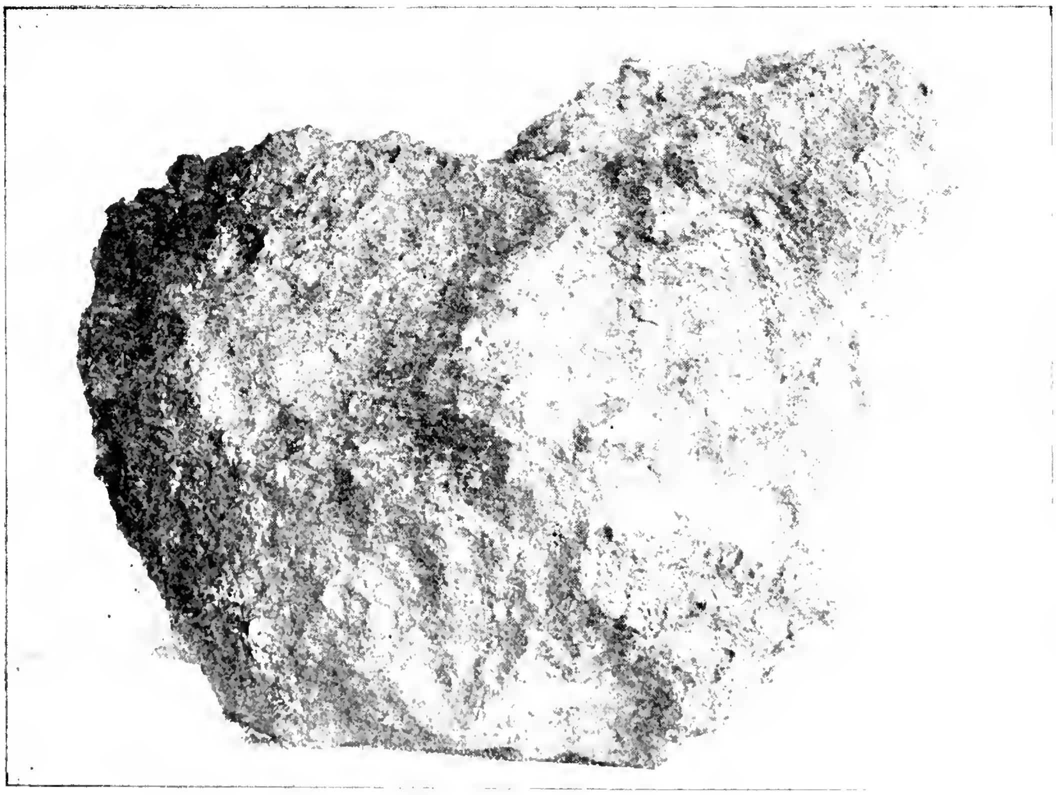

FIG. 2. — KIOWA COUNTY PALLASITE IN HARVARD CABINET.
[Reduced to one fifth in linear dimension.]

PROCEEDINGS

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ARTS AND SCIENCES.

VOL. XXVI.

PAPERS READ BEFORE THE ACADEMY.

I.

THE PREHISTORIC AND KIOWA COUNTY PALLASITES.

By Oliver Whipple Huntington, Ph. D.

Presented April 8, 1891.

In the Harvard Collection of Meteorites there is a small specimen of a pallas iron which is very highly prized as having the oldest authentic record. It is the main portion of a specimen which was found by Prof. F. W. Putnam in 1883 on the altar of Mound No. 4 of the Turner Group, in the Little Miami valley, Ohio. Therefore it is entered in the Harvard Catalogue as "Prehistoric." Ever since the acquisition of this Prehistoric specimen, specialists have been interested in trying to identify the main mass from which the smaller individual must have come. Figure 1, Plate I., shows the specimen of nearly its natural size as it came from the mound.

When the meteorite was first placed in the Harvard collection, the author of this paper made a careful study of the character and arrangement of the various constituents of the mass, thinking it possible that it might be identified with some of the pallas irons from the desert of Atacama, South America, which it appeared to resemble, thus indicating that the old builders of the mounds had visited that part of the world at some period in the remote past, and had brought away the meteorite as a sacred object sent from Heaven. As is well known, meteorites have been worshipped in very early times, and, since this identical specimen was found on an altar, it must have been highly prized, if not an object of adoration. The result of the examination, however, showed that the Prehistoric iron differed in some of its most essential characters from all the South American specimens. It did, on the contrary, resemble most strikingly the famous Siberian meteorite from Medvedeva, Krasnojarsk, which has given the name of its finder, Pallas, to that class of meteorites in which the iron forms a continuous network enclosing grains of transparent green or yellow olivine. Notwithstanding the close resemblance of the Prehistoric and Pallas irons, as the localities were so widely separated, it seemed improbable that they could have come from one and the same original mass.

In 1880 a meteorite was found in Carroll County, Kentucky, and, since it contained iron and olivine, it was at once described as the probable origin of the Prehistoric mass, since no other olivine meteorite had up to that time been found in this country.* The diagrams, however, published at that time showed that the two irons did not even belong to the same class, since the Carroll County consisted of olivine surrounding small masses of iron, while the Prehistoric was a true pallasite, consisting of iron enclosing olivine; and in the further details of the specimens there appeared to be no resemblance whatever. This fact has since been admitted; and more recently, since some very remarkable pallas irons were found in Kiowa County, Kansas, these have been claimed to be the original masses from which the Prehistoric came.†

One of the Kiowa County specimens was obtained from Prof. F. W. Cragin of Washburn College, Iowa, for the Harvard Cabinet. On a hasty examination, the resemblance of the mass to the Prehistoric iron appeared very striking. A further study, however, brought out certain features which are quite unique and worthy of description, and at the same time led to the conclusion that the resemblance to the Prehistoric meteorite was not so remarkable as it at first appeared; while, on the other hand, a further comparison of the Prehistoric with the Pallas iron again showed the two to be almost identical, as already stated.

The mass from the Kiowa County find now in the Harvard collection weighs one hundred and twenty-six pounds. It has a more

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* Am. Jour. Sci., Vol. XXXIII., March, 1887, p. 228.

† Science, Vol. XV. No. 384, June 13, 1890, p. 359.

or less ragged outline, as shown in Figure 2, Plate I., which is a reproduction from a photograph, much reduced; and the striking outline of a human profile on the right-hand upper corner suggests the possibility that it might have been taken for an image of a god. Its dimensions are, length fifteen and a half inches, height twelve and a half inches, thickness ten inches. The exterior is deeply pitted, and shows signs of fusion, as if the specimen had reached the earth as a complete individual. Its internal structure consists throughout of a continuous network of iron, enclosing grains of more or less transparent green olivine. In certain portions, as would be expected, the olivine has become somewhat altered by weathering. One spur of the mass has been sliced, and the slabs show in the unexposed portions beautiful crystals of transparent green olivine. The surface exposed by sawing has an area of about ninety square inches, and exhibits some striking variations in its different parts. Some of the olivine appears in two distinct zones, the outer portion being so dark colored that at first sight it appears by reflected light to be black, and on the large section just mentioned this apparent dark olivine occurs most abundantly around the outer edges of the section, extending in some cases an inch or more into the interior of the mass. But it is still more noticeably distributed along a crack, which extends irregularly through the mass and divides the large cut surface into nearly equal halves. This crack is followed throughout its entire length, a distance of ten inches, by an abundant deposit of the dark olivine, the grains being separated from one another by deposits of troilite, while at a short distance from the crack on either side occurs transparent green olivine, wholly distinct from the dark variety, and here the troilite is less abundant. In the original description of the Kiowa County meteorites the peculiar appearance of the olivine is described as follows: "Many of the olivine crystals are in two distinct zones, — the inner half a bright transparent yellow, the outer a dark brown iron olivine. In reality this dark zone is an intimate mixture of the troilite and the olivine, as the analysis of Mr. Eakins and a microscopical examination of the crystals by Mr. J. S. Diller of the United States Geological Survey fully proved."* This description, however, does not notice what is perhaps the most striking feature of the dark olivine, namely, that it is so strongly magnetic that lumps of considerable size will readily jump to an ordinary horseshoe magnet. Since olivine is not attracted by the magnet, and most troilite only feebly so, and pure troilite not at all, it seems hardly pos-

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* Science, Vol. XV. No. 384, June 13, 1890. p. 361.

sible that a simple mixture of the two should become as magnetic as magnetite.

On referring to the analysis made by Mr. L. G. Eakins in the laboratory of the United States Geological Survey, it appears that the composition of the dark olivine somewhat resembled that of hyalosiderite, — a variety of olivine which might be strongly magnetic. The question then arose as to whether the zone of dark olivine owed its magnetism to the composition of the olivine, or whether it was due to an admixture of a magnetic variety of sulphide of iron.

It was very difficult to obtain pieces of the dark olivine free from veins of troilite, but with sufficient care quite large fragments could be picked out, which under the microscope showed a somewhat resinous lustre, and a color varying from black and opaque to transparent red and yellow or colorless, but with no signs of any characteristic grains of troilite. After grinding the material to powder, the darker specks could be separated by the magnet, leaving the light transparent part. The magnetic portion thus selected would gelatinize with acid, but also invariably would give the reaction for sulphur, although showing no other characteristics of troilite even when examined in a thin section under the microscope. The same material was found in the Pallas and Prehistoric specimens, though of a still darker color and giving a far stronger sulphur reaction. When it became evident that the sulphur was a constant accessory of the magnetic olivine, it precluded the possibility of the olivine being a distinct variety, like hyalosiderite.

The distribution of the dark olivine mainly near the exterior of the mass and along the crack, with only occasional patches in the interior, would suggest its being an alteration product. This appeared still more probable after examining a thin section of one of the dark olivine crystals. It was seen at once that the crystals of olivine were intact except for a dark deposit along the cleavage cracks. Where the dark portion bordered on the green, the olivine was somewhat discolored, red or yellow, but evidently it had not undergone any change from weathering. It seemed more as if the dark portion had been fused and drawn into the cracks of the olivine. Experiments were therefore made to see what the effect would be of fusing the olivine and troilite of the Kiowa County pallasite, and it was found that, if non-magnetic troilite and crystals of transparent green or colorless olivine were heated together out of direct contact with the air, and the temperature raised to near the melting point of the olivine, the troilite would turn black, become strongly magnetic, and permeate all the cracks of the olivine, while portions of the olivine near the troilite changed to various shades of red and yellow, the darker portions being strongly magnetic. Otherwise, the olivine retained all its former characteristics of crystalline form and cleavage. Moreover, portions of the artificial product could be selected which would so closely resemble similar specimens from the meteorite, that, after they had been once mixed together, they could not be distinguished. This seemed to show conclusively that the dark outer zone of olivine is a mixture of troilite and olivine only in the sense above indicated.

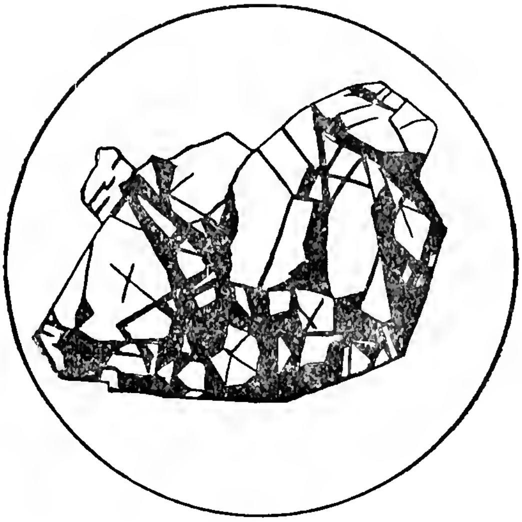
On an examination of the slabs of this iron by etching, certain other features appear which in part connect it most closely with the Pallas and Prehistoric irons, and in part are peculiar to the Kiowa County iron alone.

The olivine crystals are in the first place surrounded by a deposit of what is probably the purer iron. This border is of varying thickness, not generally exceeding one or two millimeters, and occasionally wholly disappearing. Parts of the border are most beautifully marked by innumerable Neumann lines, microscopically fine, and so numerous as to give it a silvery appearance and a brilliant lustre that at once strike the eye. Between this iron border and the olivine come masses of troilite, and these fill the space between the olivine crystals, and thus have the same kind of outline as the iron network, and appear as a continuation of the network. Troilite, however, also occurs in small nodules in the iron itself, and sometimes again as the central portion of an olivine crystal. Such a quantity and distribution of the troilite appear in no other meteorite except the original Pallas. A further resemblance between these last named meteorites is brought out in the occurrence of schreiberseit. This mineral is at once distinguished by the eye from the troilite, on account of its brighter lustre, granular structure, and more silvery color. Furthermore, it is harder, and strongly magnetic. The schreiberseit occurs in close connection with the troilite, usually in patches coming between it and the iron, but frequently portions of schreiberseit project into the iron itself, sometimes in elongated masses reaching a length of half an inch or more. In such cases the iron bordering on the schreiberseit has the same characters as when in contact with the olivine crystals, as just described.

The main portions of the iron show a most perfect crystallization, which is very beautifully brought out by etching. Crystal plates start out from the iron border already mentioned, and reach back through the whole extent of the interior iron. The figures thus produced are finer and sharper than those of any other specimen in the Harvard collection. They consist of thin plates closely packed together, not exceeding half a millimeter in thickness, but sharply defined by their border lines of bright nickeliferous iron. These plates as seen in section exhibit beautiful Neumann lines, the same as the border iron previously described, and appear to be of a piece with it. A slight suggestion of a similar crystallization is given by the Pallas iron, but the specimen at the author's disposal is not large enough for a thorough comparison. In cutting the large Kiowa County mass, the saw passed through portions of iron of considerable area, and in etching one of these nodules the plates were brought out in their greatest perfection.

The appearance of the Widmanstättian figures is best shown by Figure 3, Plate II., which is printed directly from the iron. Unfortunately, the printing does not bring out the Neumann lines on the border iron, though they are suggested in some parts of the illustration, but the general character and distribution of the Widmanstättian plates is very fairly shown. One peculiarity, however, does not exist in the slab from which the plate was printed, and though it only occurs in two or three places, yet, as it has not been observed in any other meteorite, it is worthy of note in this connection. Ordinarily in the pallasites the olivine is surrounded by a layer of iron, as if the iron had been deposited on the olivine as a nucleus; but in some of the specimens of the Kiowa County the plates of iron which form the Widmanstättian figures actually project into the olivine crystals, as if the two had solidified simultaneously. It is common here, as in other pallasites, for little plates of iron to separate two crystals of olivine; but in the specimen under discussion there are cases where the Widmanstättian plates cross the natural boundary line of the iron and project out into the olivine crystals, and intersect each other at the octahedral angle apparently wholly independent of the presence of the olivine. Occasionally, too, a little plate of iron is seen isolated from the rest, and in the very centre of a nodule of olivine. No cases were observed where the Widmanstättian plates actually cut through the olivine crystals so as to connect with the iron on the opposite side, but they projected into the crystals several millimeters.

Finally, by far the most striking and characteristic feature of the Kiowa County pallasite is the abundant occurrence of chromite. This mineral is easily confused with the dark olivine described in an earlier part of this paper, since the mode of occurrence is exactly the same, and on a polished surface the only difference is that the chromite has a more metallic lustre, and is more opaque. Chromite is widely distributed through the meteorite intimately mixed with olivine, although in some cases large crystals of clear green olivine are to be found embedded in the chromite. In several places masses of nearly pure chromite of more than an inch in diameter appear, intersected by the network of iron with its accompanying troilite and schreiberseit, the chromite largely replacing the olivine. This mixture of chromite and olivine appears as a whole perfectly black and opaque, breaking with a subconchoidal fracture, and having a brilliant submetallic lustre. It is strongly attracted by the magnet, and differs most markedly from the dark olivine before described in being perfectly opaque, and the powder is dark brown or black where in the former case it was gray.



SECTION OF OLIVINE CRYSTAL SHOWING CHROMITE.

A perfect octahedron with an axis of about two millimeters was broken out from one of these masses, but in most cases the chromite took the form of the olivine. The cause of this will be evident by reference to the accompanying figure, which represents a microscopic section of a black perfectly opaque and strongly magnetic lump of this material, the diagram having been drawn from the microscope by means of a camera lucida. It will be seen at once that, instead of its being a homogeneous substance, it proved to be a section of a transparent crystal of olivine which had had all its cleavage cracks well filled with chromite. Under the microscope, the chromite is still perfectly opaque even in such a thin section, and has a noticeably metallic lustre, with no gradual change from dark to light, as was the case in the other variety of dark olivine.

On examining the specimens of the Prehistoric and Pallas irons in the Harvard collection, no chromite was found, though of course the absence of it in those particular specimens cannot be taken as conclusive evidence of its absence in all; but it may be safely said that it would be impossible to select equally large specimens from the Kiowa County iron which would be free from this mineral.

In comparing the three pallasites, Prehistoric, Krasnojarsk, and Kiowa County, we obtain the following results.

First. All three have the dark olivine, strongly attracted by the magnet, appearing near the outside of the specimen, and frequently surrounding the clear green variety.

Secondly. All have a striking border of iron surrounding the olivine, showing a silvery sheen from the innumerable Neumann lines.

Thirdly. All show signs of Widmanstättian figures in the groundmass of the iron.

Fourthly. The Krasnojarsk and the Kiowa County both have a large quantity of troilite between the crystals of olivine, and also patches of schreiberseit between the troilite and the iron, and occasionally included by the iron. This same character appears, but in a much less degree, in the Prehistoric.

Fifthly. The Krasnojarsk and Kiowa specimens further show a much larger proportion of iron than the Prehistoric, though closely resembling each other in that respect. Figure 4, Plate II., shows a slab of the Prehistoric, printed directly from the iron.

Sixthly. The Kiowa County iron shows a very striking and far more perfect crystallization than any other pallasite heretofore described, so that if Widmanstättian figures can be used at all as a means of distinguishing irons of different falls, then the Kiowa County is distinct from any meteorite thus far described.

Lastly. The Kiowa County pallasite contains large quantities of chromite distributed through it, completely permeating large masses of the olivine, but no chromite is to be found in the Prehistoric iron or in the specimens of the Pallas meteorite in the Harvard collection.

In the description of the Kiowa County iron already referred to, the analysis and specific gravity of the olivine of the Prehistoric are compared with those of the Kiowa County as a proof of the identity of the two; but a glance at the following table will show that the analysis of the Kiowa County olivine shows a still closer resemblance to the olivine from the Pallas meteorite, and also that from Mount Etna.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	NiO	MnO	MgO	H_2O	Total.	Sp. Gr
Kiowa County	40.70	tr.	0.18	10.79	0.02	0.14	48.02		99.85	3.376
Etna	41.01	0.64		10 06	0.20		47.27	1.04	100.22	3.334
Pallas	40.83	tr.		11.53		0.29	47.74		100.39	3.334
Vesuvius . . .	40.35			12.34			46.70		99.39	
Mt. Somma .	40.08	0.18		15.26		0.48	44.22		100 24	
Prehistoric . .	40.02			14 06		0.10	45.60		99.78	3.336
Atacama . . .	36.92			17.21		1.86	43.90		99.89	3.330
Antuclo, Chili	40 70			19.60			39.70		100.00	

Furthermore, since the specific gravity of olivine only varies from 3.33 to 3.56, it is not surprising that the specific gravity of the Kiowa County and Prehistoric olivines should be so nearly alike; but it will be seen by the above table that it differs from the Prehistoric more widely than the latter differs from the other volcanic olivines. The above table could be largely extended, but enough is given to show that the olivine from the Kiowa County meteorite more closely resembles some modern volcanic products and the original Pallas meteorite, than it resembles the Prehistoric. Furthermore, when the difficulty of obtaining an average sample of meteoric material for analysis is borne in mind, it will be seen how useless it is to compare the analyses as a proof of the identity of any meteorites, and particularly the olivine ones. But the same difficulties lie in the way of giving undue weight to the etched figures or structure of a small specimen. For instance, the well known meteorite that fell at Estherville, Emmet County, Iowa, is made up largely of olivine, the iron in most specimens not forming a continuous network; yet portions can be selected almost entirely free from iron, and others where iron forms much the larger part. Figure 5, Plate II., is printed directly from an iron nodule taken from the Estherville meteorite, and placed here for comparison with the similar mass shown in the Kiowa County slab. It will be seen at once that the etched surfaces of the two irons show utterly different Widmanstättian figures. Yet the Estherville specimen does not exhibit any of the peculiar characteristics which we are in the habit of associating with that iron, and the slab from which Figure 5 is printed might be mistaken by an expert for at least half a dozen typical Widmanstättian irons, while the olivine iron to which it really belongs would be one of the last to be compared with it.

A similar feature appears even more strikingly on comparing the specimens found in Kiowa County. The largest of these has throughout the structure typical of the pallasites, but several of the smaller masses consisted wholly of iron exhibiting a highly developed crystalline structure, and in one at least, which passed into the possession of Mr. Howell of Rochester, N. Y., one end of the mass was pure iron while the rest was pallasite. We give a figure of an etched slab of this last mass, Figure 6, Plate III., which is printed directly from the iron. When first found, one was inclined to believe that the irons and the pallasites so closely associated over an area hardly exceeding sixty acres could not have come from the same fall. and this opinion seemed supported by the greater coarseness of the Widmanstättian figures on the sections of the isolated irons; but such association as is exhibited in Figure 6, Plate III., makes the intimate connection evident, and gives evidence in favor of the theory which regards meteorites as resulting from intensely violent volcanic outbursts on the surface of a planet so far cooled that the still melted nucleus was coated with an earthy crust, through which the surface water as it condensed percolated to the molten interior. By the resulting violent eruptions, of which we can form only a faint conception from terrestial volcanoes of the present day, this crust would be fissured on long lines of least resistance, and volcanic bombs thrown into space beyond the sphere controlled by the planet's attraction. Those bombs which came from the zone of contact of the melted iron with the crust would naturally have the structure of pallasites, mixed with masses consisting wholly or chiefly of metal. The specimen from which Figure 6 is printed seems to furnish the link needed to connect the stony with the iron meteorites, and if the iron portion be compared with the iron in Figure 3, Plate II., from the same fall, it will be seen of how little value the appearance of the etched surfaces would be in identifying selected portions from the two slabs.

The result of this discussion merely shows the impossibility of identifying these pallasites, which at first sight appear so much alike. If the Kiowa County specimens are accepted as identical with the one from the mounds, then both must be the same as the one from Krasnojarsk, Siberia, without further question; but the striking occurrence of chromite in such unusual quantity in the Kiowa County mass would seem sufficient to place that by itself, while leaving the close resemblance between the Prehistoric and Krasnojarsk pallasites as yet unexplained.

The question naturally arises as to the possibility of the mound builders having actually brought the Prehistoric specimen from Siberia as a sacred object. This is scarcely probable. It is well known from the writings of various authors that the inter-tribal traffic of the

American Indians was very great, and that they occasionally made journeys completely across this continent, as, for instance, the journey of Moncacht-Apé,* together with others fully as remarkable and perhaps more authentic. Moreover, Margry writes: "Il nous disoit, dans la Bibliothèque du Roy, à feu M. Thevenot et à moy, qu'il estoit dans la mesme opinion, et cela d'autant plus que le Père Martini luy avoua, en la Chine, qu'il avoit confessé en espagnol une femme Mexiquaine, qui, ayant esté enlevée esclave au Mexique, estoit arrivée de pays en pays, de nation en nation et d'esclavage en esclavage, en la Chine, par terre, sans avoir passé qu'un petit détroit de mer, et cette histoire est rapportée dans le cinquiesme volume in-8° en italien, avec figures de Giro del Mondo, du docteur Gemelli, Napolitain, arrivé depuis un an à Naples, d'où je me suis fait venir ce livre en six volumes." †

If this could be believed, it might be possible that the Prehistoric iron had found its way across Behring Straits till finally it was collected, with the other relics from all parts of this country, on the altar of Mound No. 3 of the Turner Group in Little Miami Valley, Ohio. Unfortunately for this solution, Prof. F. W. Putnam considers that the people who built the mounds came from the south. That they may have at one time had communication with China seems probable from the frequent occurrence of specimens of jadeite among their implements, and from the fact that in most cases the jadeite implements have been subsequently cut up into ornaments, while the nephrites have been left intact, showing that the former must have become more and more rare and highly prized as they were passed down through successive generations.

Provided that the original owners of our Prehistoric meteorite had associations with China, still there is no reason for supposing that they had any communication with Siberia. Nevertheless, can it be considered much more remarkable that a Siberian meteorite should be found on an altar in an Ohio mound, than that a pipe of the red indurated clay, found only on the Pipe Stone Branch of the Little Sioux River of the Missouri, should be picked up on the banks of the Rio de la Plata in South America, and several more in New England? ‡

The only other explanation of the close resemblance between the Prehistoric iron and the original Pallas would be that they were two portions of the same meteoric outburst which fell at remote distances

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* Proc. Am. Antiquarian Soc., April 25, 1883.

† Découvertes de l'Amerique Septentrionale, 1614–1754, Vol. VI. p. 173.

‡ Long's Expedition, Vol. I. p. 31.

from each other, possibly in two hemispheres, though as yet the most distant places in which the same meteorite has been identified are Mexico and Kentucky.*

The subject is an interesting one, and could be discussed at much greater length than the limits of this paper will allow, but the only object of this discussion has been to show that there is a wonderfully close resemblance between the Prehistoric and Pallas iron, and that, though the Prehistoric resembles the Kiowa County far more closely than it does the Carroll County, yet there is no reason for regarding them as identical.

In this discussion the Harvard mass of the Kiowa County find has been compared with another specimen from the same, described in a paper previously quoted as if the two were identical, and, in closing, the author would mention that he has had the opportunity of examining the various specimens in mass, and also the cut slabs placed side by side, and they are unquestionably the same.

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* Proceedings of this Academy, Vol. XXIV. p. 30, October, 1888.

Plate II.

Fig. 3. — Kiowa County, Printed directly from the Slab.

Fig. 4. — Prehistoric, Printed from the Iron.

Fig. 5. — Printed from Estherville Nodule.

PLATE III

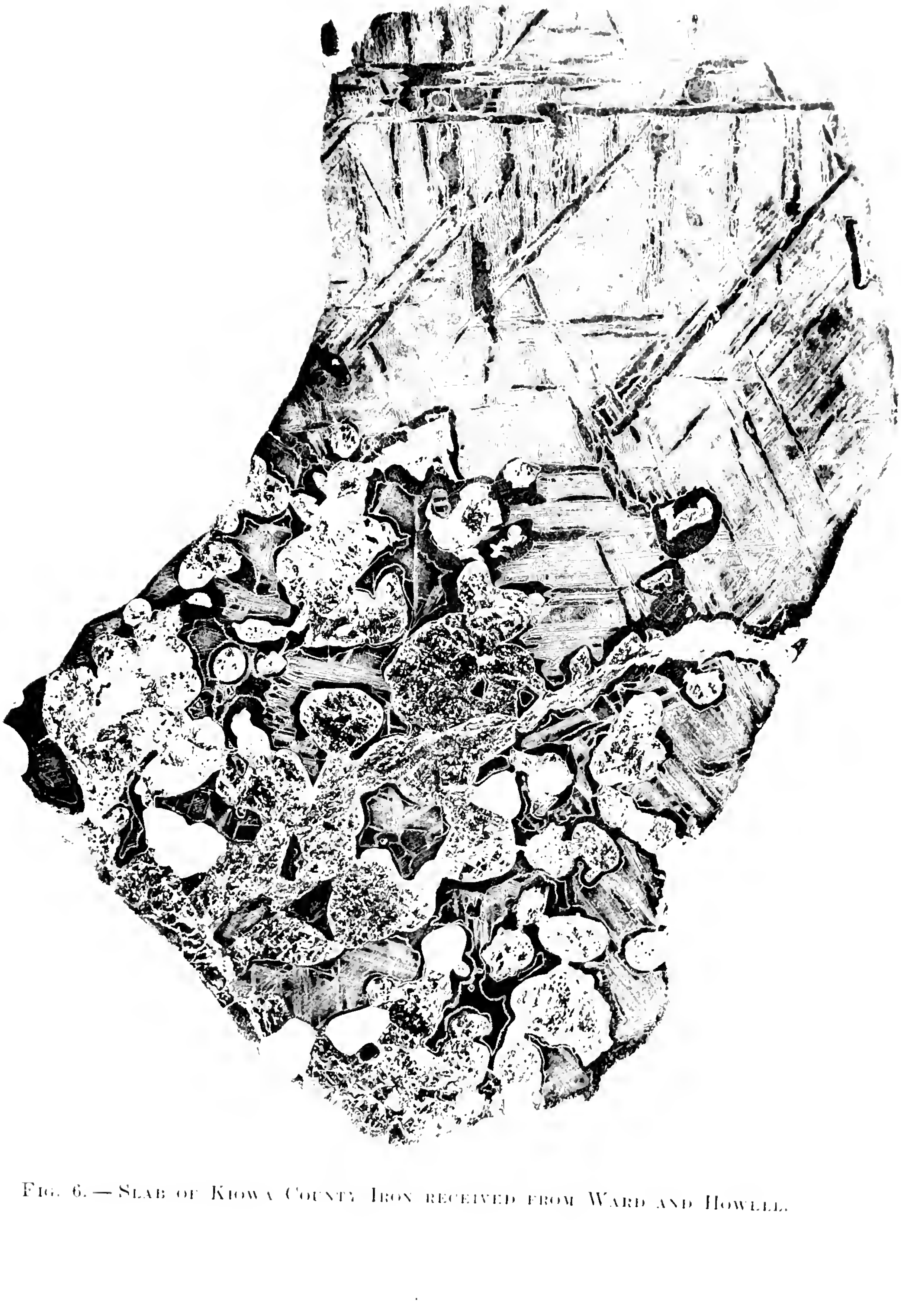

FIG. 6. — SLAB OF KIOWA COUNTY IRON RECEIVED FROM WARD AND HOWELL.

II.

PRELIMINARY NOTES ON THE SPECIES OF DOASSANSIA, CORNU.

By William Albert Setchell.

Presented March 11, 1891.

The genus *Doassansia* was established by Cornu, in 1883,[*] to receive the *Sclerotium Alismatis*, Nees, on *Alisma*, and a new species, *D. Farlowii*, on *Potamogeton*. Since then there have been several additions both of old and of new forms, until at present the number of species referred to it is twelve. All of them inhabit hosts which are more or less aquatic in habit, though belonging to widely separated families. They are said to differ little in structure, but to be distinguished from one another chiefly by the differences of the host plant.[†] A careful study of the species distributed in the various "Exsiccati," as well as of the accessible living material, has shown that this is not strictly correct. Not only are most of the species fairly well characterized by peculiarities of structure, but there are also several types of structure sufficiently diverse to be given subgeneric or even generic rank. Moreover, by the discovery of several new species, additional types of structure have been found, and have rendered it even more necessary that a careful revision of all the species should be made. On this account, full descriptions and figures of all the species of which material was available have been prepared, but as there is a delay in publication, it has seemed best to give a brief summary of the results in the present preliminary notice.

The spores of the *Doassansiæ* resemble those of the species of *Entyloma* both in structure and in germination; but in the former they are collected and compacted into balls, called by most writers "sori." The species of the genus *Doassansia* have in addition a coat, or "cortex," of sterile cells surrounding the sorus. Cornu certainly

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[*] Ann. Sci. Nat., ser. 6, Tom. XV. p. 285.

[†] Cf. Schroeter, Pilzfl. Schles., p. 286, 1887. De Toni, Journ. Myc., Vol. IV. p. 14, 1888.

considered that the possession of this cortex was the distinguishing feature of the species of his genus, although, as will be noted under *D. Farlowii*, he did not always recognize the true cortex. It seems best, therefore, to refer to *Doassansia* all the species of the group of the *Entylomata* which have the sorus invested with a cortex of sterile cells.

The sori of several species referred to *Doassansia* show, when thin sections are examined, that this cortex is not present. Such are the sori of *D. Niesslii*, De Toni, *D. Limosellæ*, (Kunze), Schroeter. *D. decipiens*, Winter, and an undescribed form on *Echinodorus rostratus*, mentioned by Harkness under *D. Alismatis*.* These several species, together with *Entyloma crastophilum*, Sacc., and probably others, form a group intermediate between the simpler species of *Entyloma* and those of *Doassansia* proper; but the limits of this group cannot be ascertained with any exactness without a careful study of all the numerous forms which of late have been referred as species to *Entyloma*. They must therefore be left unsettled in position for the present.

Among the *Doassansiæ*, as is the case among the *Entylomata* in general, the specific distinctions are not striking. They differ slightly in habit when dried, yet when fresh most of the species may be distinguished at a glance by the peculiar distortion or discoloration of the host plant produced by them. As a rule, the *Entylomata* do not produce distortions, but two of the species of *Doassansia* cause swellings of considerable size. The structure of the sorus varies decidedly, and has been made in these notes the basis of generic and subgeneric distinctions. The germination has been obtained wherever possible, and has been found to vary in its details among the different species.

Following is given the arrangement of the species and genera.

DOASSANSIA, Cornu.

Spores resembling those of *Entyloma* both in structure and in germination, collected and compacted into sori. Cortex of sterile cells present.

Subgenus I. Eudoassansia.

Body of the sorus consisting entirely of spores, which are readily separable from one another at maturity.

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* Cf. Proc. Cal. Acad. Sci., ser. 2, Vol. II. p. 231, 1889.

The type of this subgenus is *D. Alismatis*, Cornu, which represents Cornu's idea of *Doassansia.*

1. *D. Epilobii*, Farlow.
On leaves of *Epilobium alpinum.*
United States !
The cells of the cortex of this species are very small and flattened, and the sori, on this account, very closely resemble those of *D. decipiens*, Winter. It may perhaps be looked upon as a form intermediate between the group represented by *D. decipiens* and the group of the *Eudoassansiæ.*

2. *D. Hottoniæ*, (Rostr.), De Toni.
On leaves of *Hottonia palustris.*
Denmark !, Germany !, France !.

3. *D. Sagittariæ*, (Westend.), Fisch.
On leaves of *Sagittaria sagittifolia*, *graminea*, *variabilis*, and *Montevidensis.*
Italy !, France !, Germany !, Belgium !, England ! ; Argentine Republic ; Canada !, United States !.

4. *D. opaca*, sp. nov. Spot orbicular, slightly swollen on both surfaces of the leaf, lemon-yellow, at length dark brown and opaque. Sori crowded, indistinct when viewed with a lens, globular to almost cubical, 200–300 μ by 80–100 μ, light brown. Spores rather loosely compacted together, nearly spherical, 10–15 μ in diameter. Cortical cells of various shapes, from brick-shaped to almost cubical. Germination unknown.
On leaves of *Sagittaria variabilis.*
United States ! (Newton, Mass., *W. G. Farlow !*, Medford, Mass. !, Norwich, Conn. !).
This species was mentioned by Farlow * under the name of *Protomyces Sagittariæ,* as occurring at Newton, Mass. The same form has been collected by myself, both at Medford, Mass., and at Norwich, Conn., in abundance, and has been studied in all stages of development. The species differs decidedly from *D. Sagittariæ* in habit and form of the sorus, as well as in the character of the cortical cells. Sowings of the spores have been repeatedly made, but the germination, unfortunately, has not been obtained. The species is readily detected by holding an infected leaf between the eye and

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* Bot. Gaz., Vol. VIII. p. 276, August, 1883.

the light, when the spots appear as dark, black patches in the leaf substance.

5. *D. Alismatis*, (Nees), Cornu.

On leaves of *Alisma natans* and *Plantago*.

Italy !, France, Germany !, Finland !, England !; Siberia !; United States !.

SUBGENUS II. PSEUDODOASSANSIA.

Central portion of the sorus composed of an irregular-shaped mass of fine, densely interwoven hyphæ. Spores in several layers, loosely compacted together. Cortex of large, well differentiated cells.

6. *D. obscura*, sp. nov. Spot none. Sori in lines in the larger intercellular spaces at the base of the petioles and peduncles of the host, globular to ellipsoidal, 180–220 μ by 200–300 μ, light brown. Spores almost globular, 8–12 μ in diameter, light-colored. Cortical cells obversely conical, conspicuously lobed at the outer, broader end. Promycelium narrowly cylindrical, about 20 μ long. Sporidia in whorls of 5 to 7, elongated fusiform, 16–17 μ long and 1.5–2 μ thick, producing bunches of secondary sporidia without conjugation.

On petioles and peduncles of *Sagittaria variabilis*.

United States ! (Cambridge, Mass. !, Medford, Mass. !, Norwich, Conn. !).

This species is very inconspicuous, being detected only upon the most careful examination. When occurring upon the green portions of the petioles and peduncles, it causes a very faint yellowish discoloration. It most frequently inhabits the white portions at the very base of these parts, and then the dark lines of sori show through the more or less transparent outer tissues. It is abundantly distinct from all the other species of the genus. The central hyphæ, the loosely compacted spores, the obconic lobed cells of the cortex, and the method of germination of the spores, are all characteristic. It seems to differ so much from the species which cluster about *D. Alismatis* as to demand a special subgenus for its reception.

SUBGENUS III. DOASSANSIOPSIS.

Sorus compact, not separating into its component elements at maturity. Central portion consisting of a compact mass of parenchymatous tissue. Spores in a single layer. Cortex of small flattened cells.

7. *D. occulta*, (Hoffm.).

D. occulta, (Hoffm.), var. *Farlowii*, (Cornu).

Authentic specimens of *D. Farlowii*, Cornu, do not seem to me to correspond exactly to Hoffmann's figures,* but differ particularly in having spores which are elongated in a radial direction. Specimens collected by myself near Norwich, Conn., agree better with Hoffmann's figure, and are considered in these notes to represent the type of *D. occulta*, while *D. Farlowii* is for the present placed as a variety under it. The elongated cells on the periphery of the sorus in Cornu's figure † are really the spores, and the real cortex of small, radially flattened cells is not shown, while the rounded cells in the centre are not immature spores, but are sterile cells resembling parenchyma cells.

In the ovaries of species of *Potamogeton*.

Type. Germany; United States! (Norwich, Conn.!).

Var *Farlowii*. Canada (Ottawa, *J. B. Fletcher!*).

8. *D. Martianoffiana*, (Thuem.), Schroeter.

On leaves of species of *Potamogeton*.

Siberia; Germany, Sweden!; Canada!.

In the specimens from Sweden, distributed by Johanson, ‡ there appear to be conidia, almost identical in appearance with those already known in some species of *Entyloma*. There seems to be an intimate connection between the mycelium of the *Doassansia* and that of the conidia.

9. *D. deformans*, sp. nov. Species forming distortions, often of large size, on all parts of the host. Sori globular, 100–140 μ, very light brown. Spores polyhedral, 8–10 μ by 4–8 μ. Cortical cells polygonal, flattened radially. Promycelium somewhat obconical, about 12 μ long. Sporidia 5 to 6, broadly fusiform, 12 μ by 4–5 μ, conjugating and producing a short germ tube.

In the leaves, petioles, peduncles, pedicels, and ovaries of *Sagittaria variabilis*.

United States! (Norwich, Conn.!, Cambridge, Mass.!); Canada (London, leg. *Dearness*, comm. *J. B. Ellis*).

A species forming large distortions on *Sagittaria*, nearly related to the other species of the subgenus, but abundantly distinct from all the

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* Ic. Anat. Fung., Taf XVI. Fig. 3, 1862.

† Ann. Sci. Nat., Tom. XV. Pl. XVI. Fig 6, 1883.

‡ Cf. Eriksson, Fung Scand. Par., No. 264, 1888. Pazschke, Fung. Eur., No. 3602, 1890.

other species on the same host. It is to be distinguished from *D. occulta* (type) by its method of germination. It is without doubt more widely spread, but the distortion is probably mistaken for the work of an insect rather than that of a fungus.

Species Inquirendæ.

10. *D. Comari*, (B. & Br.), De Toni.
On leaves of *Comarum palustre.*
England.

11. *D. punctiformis*, Winter.
On leaves of *Lythrum hyssopifolium.*
Australia.

12. *D. Lythropsidis*, Lagerh.
On *Lythropsis peploides.*
Portugal.

Species Excludendæ.

D. Niesslii, De Toni.
D. Limosellæ, (Kunze), Schroeter.
D. decipiens, Winter.
D. Alismatis, Hark. (not Cornu).

BURRILLIA, gen. nov.

Sorus compact, not separating into its elements on being crushed. Central portion composed of an irregular mass of parenchymatous tissue. Spores closely resembling those of *Entyloma*, both in structure and in germination, compacted into several dense rows. Cortex none or composed only of a thin, irregular ayer of hardened hyphæ.

B. pustulata, sp. nov. Spots irregularly orbicular, often confluent, light yellow, chiefly hypophyllous. Sori elongated ellipsoidal, at length bursting through the epidermis, which appears raised in small blisters, 200–350 μ by 150–180 μ, light brown. Spores not separable at maturity, almost globular, 4–6 μ in diameter, germinating while the sori are in position. Promycelium cylindrical, 15 μ long, bearing 4–5 sporidia in a whorl at the blunt apex. Sporidia slightly bent, 16 μ by 3 μ.

On leaves of *Sagittaria variabilis.*

United States! (Illinois, leg. *G. P. Clinton !*, comm. *T. J. Burrill*, Wisconsin, *W. Trelease !*).

The sori of this species resemble in structure the spore balls of *Testicularia Cyperi*, Klotsch.;* but the position of that species is un-

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* Cf. Cornu, Ann. Sci. Nat., ser. 6, Tom. XV. pp. 270–273, Pl. XIV. Fig. 1–5, 1883.

certain, and even if it is one of the *Ustilagineæ* at all, it belongs rather to the series of the pulverulent smuts, while the present form, both in spore structure and in germination, is closely related to *Doassansia* and to *Entyloma*. It is to be distinguished from any of the species of *Doassansia* by the lack of a cortex, and from any of the other *Entylomata* by the presence of the central parenchymatous portion. In the latter, it resembles the forms described under the subgenus *Doassansiopsis*, but it differs from them not only in the lack of a cortex but also in the possession of several layers of spores. The genus is named in honor of Prof. T. J. Burrill, of the University of Illinois, by whom the first specimens were sent.

CORNUELLA, gen. nov.

Sorus hollow at maturity, the interior containing only loose, hardened hyphæ. Spores compacted into a firm layer on the outside, resembling those of *Entyloma* both in structure and in germination. Cortex none.

C. Lemnæ, sp. nov. Spot none. Sori globular to ellipsoidal, 50–70 –100 μ in diameter, dark brown. Spores not separable at maturity, often elongated radially, 10–12 μ by 6–10 μ. Promycelium somewhat obconical. Sporidia in whorls of 5 to 7, narrowly fusiform, 26 μ by 2 μ, producing a germ tube after conjugating.

In the fronds of *Lemna* (*Spirodela*) *polyrrhiza*.

United States ! (Cambridge, Mass. !, Newton, Mass. !; Belchertown, Mass., *J. E. Humphrey !*).

The type of this genus, which I respectfully dedicate to Prof. Maxime Cornu, of the Jardin des Plantes, is very different from any described member of the *Ustilagineæ*. The hollow sorus with only loosely entangled hyphæ on the inside, is unique, and yet the spore structure and germination closely ally it with *Doassansia* and *Burrillia*.

The germination takes place while the spores are in position, and the whole sorus is covered with a bristly mass of promycelia and sporidia. Something of the same thing happens also in *Burrillia pustulata* and in the species of the subgenus *Doassansiopsis*.

III.

ON SOME THEOREMS WHICH CONNECT TOGETHER CERTAIN LINE AND SURFACE INTEGRALS.

BY B. O. PEIRCE.

Presented May 13, 1891.

IN transforming from one set of curvilinear coördinates to another, some of the differential expressions which appear in problems in Hydrokinematics and Electrokinematics, I have found the theorems[*] stated below useful.

Theorem. — Let U be any function of the two polar coördinates, r and θ, which, with its first space derivatives, is finite, continuous, and single-valued throughout that part of the coördinate plane which is shut in by the closed curve T. Let δ be the angle between the radius vector, drawn from the origin to any point P on T, and the normal to T drawn from within outwards at P. Then, if T does not include

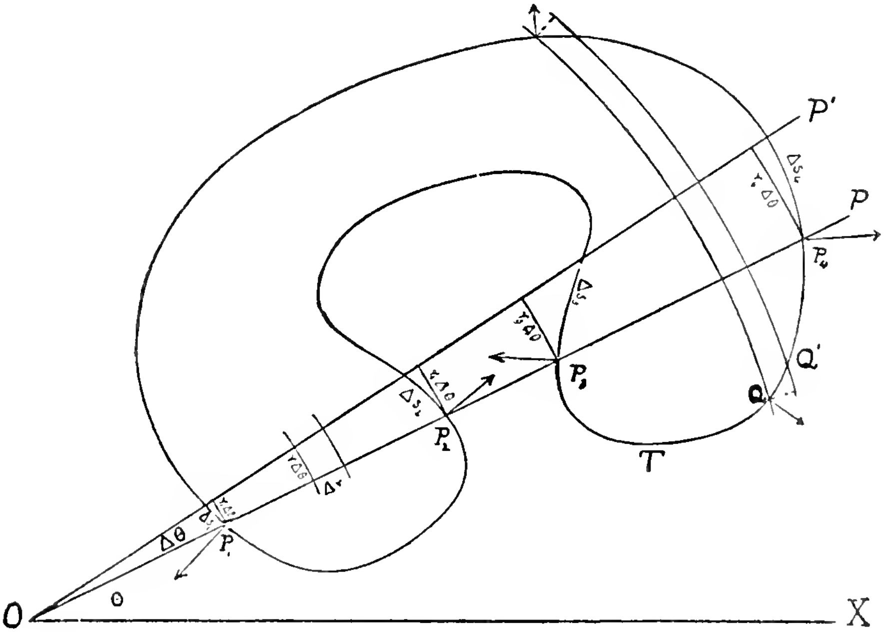

FIG. 1.

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[*] London Educational Times, January and February, 1891.

the origin, the line integrals of $U \cos \delta$ and $U \sin \delta$, taken around T, are equal respectively to the surface integrals of $\frac{D_r(r \cdot U)}{r}$ and $\frac{D_\theta U}{r}$, taken over the area enclosed by T.

For the element of plane surface in polar coördinates, $r \Delta r \Delta \theta$ may be used. Let the radius vector OP, drawn so as to make the angle θ with the initial line OX, cut T $2n$ times at points $P_1, P_2, P_3, \ldots . P_{2n}$, distant respectively $r_1, r_2, r_3, \ldots . r_{2n}$ from O. Let the values of U at these points of intersection be $U_1, U_2, U_3, \ldots . U_{2n}$, respectively. Whenever the radius vector *cuts into* the closed contour, either $+\delta$ or $-\delta$ is an obtuse angle and $\cos \delta$ is negative; whenever the radius vector *emerges from* the space enclosed by the contour, either $+\delta$ or $-\delta$ is acute and $\cos \delta$ positive. The two neighboring radii vectores, OP and OP', which make with each other the angle $\Delta \theta$, include between them the arcs $\Delta s_1, \Delta s_2, \Delta s_3, \Delta s_4, \ldots . \Delta s_{2n}$, cut out of T, and the arcs $r_1 \Delta \theta, r_2 \Delta \theta, r_3 \Delta \theta, \ldots . r_{2n} \Delta \theta$, cut out of a set of circumferences drawn about O as centre, with radii $r_1, r_2, r_3, r_4, \ldots . r_{2n}$, respectively. It is evident that, if $\Delta \theta$ be made to approach zero as a limit,

$$+ \text{Limit} \frac{r_1 \cdot \Delta \theta}{\Delta s_1 \cdot \cos \delta_1} = - \text{Limit} \frac{r_2 \cdot \Delta \theta}{\Delta s_2 \cdot \cos \delta_2} = + \text{Limit} \frac{r_3 \cdot \Delta \theta}{\Delta s_3 \cdot \cos \delta_3}$$

$$= - \text{Limit} \frac{r_4 \cdot \Delta \theta}{\Delta s_4 \cdot \cos \delta_4} = + \text{Limit} \frac{r_{2n-1} \cdot \Delta \theta}{\Delta s_{2n-1} \cdot \cos \delta_{2n-1}} = - \text{Limit} \frac{r_{2n} \cdot \Delta \theta}{\Delta s_{2n} \cdot \cos \delta_{2n}}$$

$$= -1.$$

If the double integral be extended all over the space enclosed by T,

$$\int\!\!\int \frac{D_r(rU)}{r} r \, dr \, d\theta = \int d\theta \, [- r_1 U_1 + r_2 U_2 - r_3 U_3 + \ldots . + r_{2n} U_{2n}],$$

where the integration with respect to θ is to be extended over all values of the angle for which the corresponding radii vectores cut T. If now for $r_1 \Delta \theta$, $r_2 \Delta \theta$, $r_3 \Delta \theta$, etc., $- \cos \delta_1 \cdot ds_1$, $+ \cos \delta_2 \cdot ds_2$, $- \cos \delta_3 \cdot ds_3 + \ldots . + \cos \delta_{2n} \, ds_{2n}$ be substituted respectively, we have

$$\int\!\!\int \frac{D_r(rU)}{r} r \, dr \, d\theta = \int [U_1 \cos \delta_1 \, ds_1 + U_2 \cos \delta_2 \, ds_2 + \ldots . U_{2n} \cos \delta_{2n}],$$

and this last integral is evidently equal to the line integral of $U \cos \delta$ taken all around T.

It is to be noticed that, if O were within T, each radius vector would cut T an odd number of times, and that a negative sign must stand before the line integral.

Since the limit of the ratio of Δr to any one, QQ', of the arcs cut out of T by two circumferences of radii r and $r + \Delta r$ respectively, drawn around O as a centre, is equal in absolute value to the sine of the angle which OQ makes with the external normal to T at Q, it is easy to prove the second part of the theorem by integrating $D_\theta U$ with regard to θ first, and then, after introducing proper limits, with regard to r.

This theorem may be regarded as a useful special case of the following

Theorem. — Let $\zeta = f_1(x, y)$ and $\eta = f_2(x, y)$ be two analytical functions of x and y such that the two families of curves $f_1(x, y) = c$, $f_2(x, y) = k$, are orthogonal. Let V be any function of x and y which, with its first space derivatives is finite, continuous, and single-valued within a closed curve T, drawn in the coördinate plane. Let h_1 and h_2 be the positive roots of the equations $h_1^2 = (D_x\,\zeta)^2 + (D_y\,\zeta)^2$, $h_2^2 = (D_x\,\eta)^2 + (D_y\,\eta)^2$. Then, if ζ has neither maximum nor minimum values within T, the surface integral of $h_1 \cdot h_2 \cdot D_\zeta\left(\frac{V}{h_2}\right)$, taken all over the area enclosed by T is equal to the line integral taken around T of $V \cos\delta$, where δ is the angle between the exterior normal drawn to T at any point, and the curve of constant η drawn through the point, and where the direction in which ζ increases is taken positive.

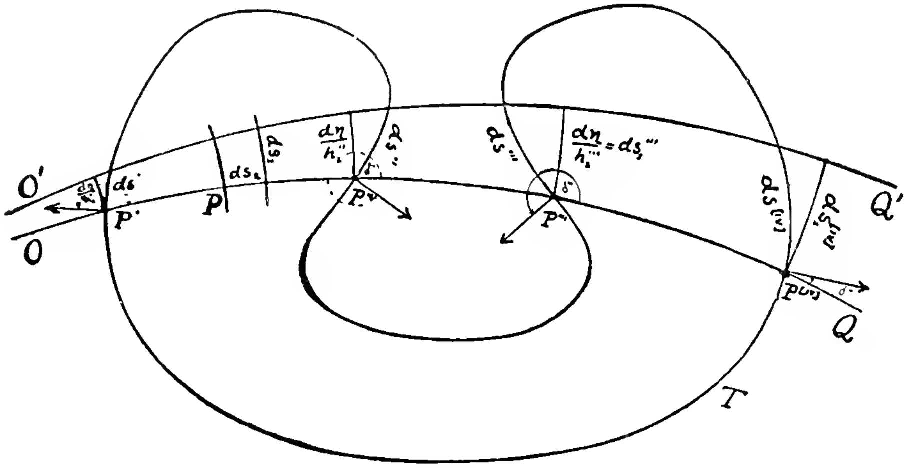

FIG. 2.

Similarly, if proper regard be had for signs,

$$\iint h_1 \cdot h_2 \;\; D_\eta\left(\frac{V}{h_1}\right)\, ds = \int V \sin\delta \cdot d\,s.$$

If through any point, P, in the coördinate plane, two arcs s_1, s_2 be drawn along which ζ and η are respectively constant, $d\,s_1 = \frac{d\,\eta}{h_2}$,

$ds_2 = \frac{d\zeta}{h_1}$, and for the element of surface $\frac{d\zeta \cdot d\eta}{h_1 \cdot h_2}$ may be used. The surface integral of $h_1 \cdot h_2 \cdot D_\zeta \left(\frac{V}{h_2}\right)$ taken over the area enclosed by T is

$$\Omega = \iint h_1 \cdot h_2 \cdot D_\zeta \left(\frac{V}{h_2}\right) d s_1 \cdot d s_2 = \int d\eta \int D_\zeta \left(\frac{V}{h_2}\right) d\zeta.$$

Consider two curves OQ, $O'Q'$ along which η has respectively the constant values η_0 and $\eta_0 + \Delta\eta$; and let ζ increase in the directions OQ, $O'Q'$.

Let OQ cut T $2n$ times at the points P', P'', P''', ..., $P^{[2n]}$, where the values of h_2 are h_2', h_2'', h_2''', ..., $h_2^{[2n]}$, respectively, and the corresponding values of V, V', V'', V''', ..., $V^{[2n]}$. The curved line OQ makes with the normals drawn to T at P', P'', P''', etc., from within outwards the angles δ', δ'', δ''', etc., and the two curves OQ, $O'Q'$, cut out of T the $2n$ arcs $\Delta s'$, $\Delta s''$, $\Delta s'''$, ..., $\Delta s^{[2n]}$.

$$\Omega = \int d\eta \left[-\frac{V'}{h_2'} + \frac{V''}{h_2''} - \frac{V'''}{h_2'''} + \frac{V^{[\text{IV}]}}{h_2^{[\text{IV}]}} - \dots + \frac{V^{[2n]}}{h_2^{[2n]}} \right],$$

where the integration is to be extended over all values of η which occur within T.

The angles δ', δ''' .... $\delta^{[2n-1]}$, or their negatives, are all obtuse and their cosines are negative, but the angles δ'', $\delta^{[\text{IV}]}$, ... $\delta^{[2n]}$, or their negatives, are all acute and their cosines are positive, so that at every point, $P^{[k]}$, where OQ cuts T we have

$$\underset{\Delta\eta \doteq 0}{\text{Limit}} \left\{ \frac{(-1)^k \cdot \Delta s^{[k]} \cdot \cos\delta^{[k]}}{\frac{\Delta\eta}{h_2^{[k]}}} \right\} = 1,$$

and in the expression for Ω we may write $(-1)^k \cdot \cos\delta^{[k]}\, d s^{[k]}$ for $\frac{d\eta}{h_2^{[k]}}$.

Hence,

$$\Omega = \int [V' \cos\delta'\, ds' + V'' \cos\delta''\, ds'' + \dots + V^{[2n]} \cos\delta^{[2n]}\, d s^{[2n]}],$$

where the sign of integration directs us to find a similar expression to that in the brackets for every pair of consecutive curves of constant η which cut T, and to find the limit of the sum of the whole. This is evidently equivalent to integrating $V \cos\delta$ all around the curve T.

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IV.

THE QUANTITATIVE DETERMINATION OF ARSENIC, BY THE BERZELIUS-MARSH PROCESS, ESPECIALLY AS APPLIED TO THE ANALYSIS OF WALL PAPERS AND FABRICS.

By Charles R. Sanger.

Presented May 13, 1891.

The original method of Marsh* was published in 1836, and in the following year Berzelius † proposed the modification which couples his name with that of Marsh. It seems to have escaped notice, at least I can find no mention of the fact, that Berzelius also suggested the quantitative application of the method. He proposed to place some pieces of copper in the reduction tube, and, after weighing tube and copper, to heat and pass the arsenical gas through. The copper would further the reduction of the arseniuretted hydrogen, and thus the arsenic might be collected and weighed. Wöhler,‡ in 1861, proposes essentially the same method, but heats the tube in two places, at the copper which he uses in the form of a spiral, two inches long, and also just behind the copper, so that whatever gas escapes decomposition by the first heating may be decomposed by the copper. The first practical application of this method seems to have been made by Gautier,§ in 1876, in the estimation of arsenic contained in tissues. He omits the copper spiral, but heats the reduction tube by a layer of charcoal 20 to 25 cm. in length. To determine the arsenic deposited, he weighs the tube, dissolves out the mirror by nitric acid, and, after drying, weighs again. Crommydis,‖ a year later, follows Gautier's method in a similar research.

Chittenden and Donaldson,¶ in 1881, investigated this method with very satisfactory results, and suggested the improvements which

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* Edin. Philos. Journ., XXI. 229.

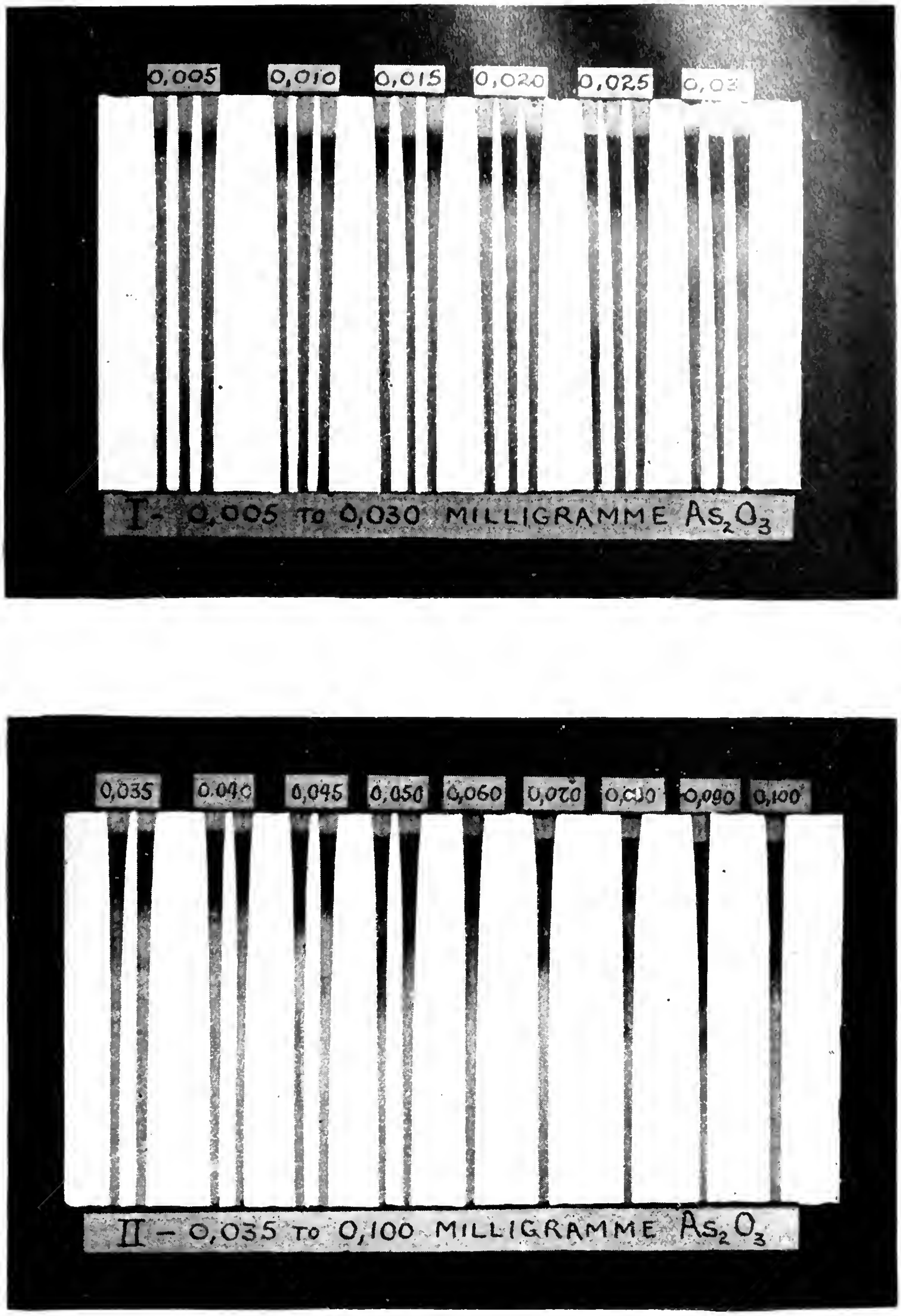
† Berzelius, Jahresb., XVII. 191.

‡ Mineral-analyse, p. 232.

§ Ann. d'Hygiène publ. et de Méd. légale, 1876, p. 136; also Bull. de la Soc. Chim., [2.] XXIV. 250.

‖ Bull. de la Soc. Chim., [2.] XXV. 348.

¶ American Chemical Journal, Vol. II. No. 4; Chem. News, XLIII. 21; Moniteur Scient. de Paris, 1881, p. 227.



QUANTITATIVE DETERMINATION OF ARSENIC BY THE BERZELIUS-MARSH PROCESS
STANDARD MIRRORS.

were necessary for its adoption as a trustworthy analytical method. Their process has found its way into the text-books, and needs no explanation here. I note its use by Hubbard* in 1882, and Prescott† in 1886, and undoubtedly many others have employed it in toxicological work. It seems remarkable, therefore, that the previous application of the process to quantitative work should have escaped the attention of Kühn and Saeger,‡ as well as Polenske,§ to whom they refer as the first to propose the method. Kühn and Saeger's article, published a few months ago, contains nothing new; but as the paper of Polenske is inaccessible to me, I cannot say what modification he may have introduced.

I need not refer here to the numerous quantitative methods which depend on the reduction by nascent hydrogen and absorption of the arseniuretted hydrogen by argentic nitrate, the eventual determination of the arsenic being made from the silver solution in a variety of ways. These methods form a class by themselves, and cannot be included in the Berzelius-Marsh process.

All methods for the estimation of arsenic are open to a common objection; they do not allow the estimation of minimal, or even, with accuracy, of small amounts. It happens so often that a small amount of arsenic must remain unestimated, because unweighable, and only an approximation to the real quantity can be made.

In the qualitative analysis of wall papers and fabrics by the Berzelius-Marsh method, much confusion results from the careless manner of reporting the amount of arsenic which makes its appearance in the reduction tube. The reports, "trace," "small amount," "large amount," are usually made without reference to any standard mirrors, time of heating the reduction tube, or, in many cases, to the amount of substance taken for analysis. On account of the want of a definite quantitative method which could be easily applied to wall papers and fabrics, there have been some propositions for a rough quantitative determination, which should serve as a control as to whether the substance contained more or less than a prescribed amount. The Swedish law ‖ of 1883, for instance, though not using the Berzelius-

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* Physician and Surgeon, Ann Arbor, IV. 348; also, Contributions from the Chem. Lab. Univ. Mich., Vol. I. Part I. p. 12.

† Chem. News, LIII. 79.

‡ Ber. d. deutsch. chem. Gesell., XXIII. 1798.

§ Arb. a. d. kais. Gesundheitsamt, Bd. V. Heft 2 (1889).

‖ Correspondence between the English and other Governments respecting the Presence of Arsenic . . . in Wall Papers and Textile Fabrics. Commercial, No. 40 (1883).

Marsh method, prescribes that "440 sq. cm. of the article . . . by reduction with potassic cyanide and sodic carbonate, shall not produce more than a partially opaque mirror in a glass tube of 1.5 to 2 mm. inner diameter." Thoms* in 1883 proposes as a means of control that the results from 100 sq. cm. of paper should be divided into four grades: "strongly arsenical," "arsenical," "traces," and "free." If, when the apparatus has been running ten minutes after the introduction of the solution to be tested, a deposit is obtained no larger than that corresponding to what is produced by 0.1 mgr. of arsenious oxide under similar conditions, the paper may be considered to contain a "trace," and need not be rejected.

A committee of the National Health Association of Great Britain, consisting of Messrs. Bartlett, Heisch, and De Chaumont,† suggested, in 1883, that a paper should be considered non-arsenical if, after being treated by a modification of the Berzelius-Marsh method devised by them, it failed to give a mirror in a tube of one eighth inch internal diameter (about 3.3 mm.) sufficient to cut off at any point a black line of a certain thickness ("thick rule, 8 to pica") on a white ground.

All this is very crude, yet, without a means of easily estimating the amount of arsenic present, it might answer until the exact determination was called for.

The length of time necessary for any of the quantitative methods precludes their use by analysts, especially when, as is generally the case, the quantitative determination is not of especial importance. If we attempt to apply the gravimetric Berzelius-Marsh method to the analysis of wall paper, we are met, not only by the amount of time necessary for the complete deposition of the arsenic mirror, but by the large amount of paper that must be taken, or, if the proportion of arsenic is very small, the unwieldy amount. Added to this is the necessity for a delicate balance, and also the error in weighing small mirrors of arsenic.

A method is therefore desirable which will allow us to estimate minimal amounts of arsenic, and, in such analyses as that of wall paper, will give an approximate idea of the amount present without requiring more time than that needed for the proper conduct of the ordinary Berzelius-Marsh method.

The process which is described in the following pages was suggested by Professor H. B. Hill of Cambridge, about five years ago,

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* Ref. Fres. Zeitschr., XXII. 474, from Ber. d. landw. chem. Vers. u. Samencontrolstat. zu Riga, 1883.

† Brit. Med. Jour., 1883, p. 1218.

and has been in use in that laboratory and others with excellent success. The proof of the availability of the method was undertaken by me, but, owing to numerous interruptions, the completion of the analytical work has been delayed until now.

The method consists, briefly, after getting the arsenic from a measured amount of paper or fabric into solution, in the comparison of the mirror obtained from an aliquot part of the solution with a series of standard mirrors obtained from known amounts of arsenious oxide. No method founded on exactly this principle has ever been fully described, though Otto * gives cuts of mirrors obtained from known amounts of arsenious oxide, with which some analysts may have compared their mirrors. Selmi,† in 1880, states that he is able to approximate to fractions of a milligram by comparing the mirrors with those obtained from the following amounts: one twentieth, one fiftieth, one hundredth, and one two-hundredth part of a milligram. Thoms, as stated above, compares his "traces" with a mirror obtained from one tenth of a milligram, and says that the mirror can be kept any length of time as a comparison standard. Blyth ‡ also suggests a comparison of mirrors.

I give in detail the method as I have used it in the analysis of wall paper, making references to the analytical and experimental work which follows.

The measurement of the paper is governed by (*a*) the quantity of arsenic present, which may sometimes be judged by the color, or by the rough test of the odor from the burning paper, and (*b*) by the character of the paper; i. e. whether a plain color, a small or large figure. I have used 25 sq. cm., 50 sq. cm., and usually 100 sq. cm. As patterns for cutting, thin plates of glass § may be used, on which are marked the dimensions. The advantage of the glass is, that the figure of the paper may be seen while the paper is being cut, and also, that, by washing or wiping the glass after each cutting, any danger of contamination by adhering particles from a previous arsenical paper may be avoided. I have used but one plate for 25 sq. cm. (5 × 5); for 50 sq. cm., three (5 × 10, 4 × 12.5, and 2 × 25); and for 100 sq. cm., five (10 × 10, 5 × 20, 4 × 25, 8 × 12.5, and 2 × 50); such a number allowing the variety in cutting that different papers necessitate.

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* Graham-Otto-Michaelis, Lehrbuch, II. 2, 520.

† Gazz. Chim. Ital., X. 435.

‡ Poisons, their Effect and Detection, 1884, p. 534.

§ Dr. Charles Harrington.

The paper, cut into small pieces, is placed in a glazed porcelain dish and moistened with 1 to 5 c. c., according to the amount of paper taken, of strong sulphuric acid (sp. gr. 1.8) to which has been added about one thirtieth of its volume of strong nitric acid (Appendix, 2. *e*). The paper and acid are stirred with a thick glass rod until the paper has absorbed the acid, and the dish is then placed on a ring and heated by a low flame, the mixture being stirred continually, until the paper is thoroughly charred (App., 1). This may be determined by the dry "crumbly" appearance, and by the amount of fuming, it being necessary to heat until the nitric acid is expelled. Usually, the first heating is enough, as, even if a trace of nitric acid is left, it does no harm (App., 2. *f*) ; yet, if one has reason to think that considerable nitric acid is held back, it is best, after cooling, to add a few cubic centimeters of water, and heat again until the fumes of sulphuric acid appear. On cooling, the "char" is moistened with a few drops of water, and then about 5 c. c. of water are added. The mass is triturated with the thick rod until all lumps are thoroughly broken up, heated to boiling to expel sulphur dioxide (App., 5. *d*) and filtered hot (App., 3).

Filtration of the Extract. — In filtering, time is saved and greater accuracy assured by using a filter pump, and for filtration I have found most convenient a sideneck test tube of 25 to 30 c. c. capacity. This is fitted with a rubber cork through which passes a small funnel, the end reaching just below the side tubulus of the test tube. With the tubulus is connected the pump, and in order to prevent accidental contamination of the tubulus, (through which the extract is afterwards poured into the Marsh apparatus,) I use a connecting glass tube, which may be rinsed before and after each filtration. This tube is a small U tube not over 25 cm. in total length, with two bulbs blown in the lower part of the U. The filter paper is of small diameter, not over 8 cm. and the lot should be tested for arsenic previous to cutting the round filters. As a strengthening cone at the apex will be found convenient for this, as well as for other filtrations, a square piece of cheese cloth laid under the paper and folded with it.

After filtering, the char is washed with small quantities of hot water until the filtrate and washings fill the test tube. The extract, after cooling, is ready for weighing or measuring, and introduction into the apparatus.

The Apparatus. — Two points will have been noticed in working with the ordinary form of generating flask: the time required for displacement of the air, and the impossibility of governing the evolution of hydrogen during the analysis. The latter objection is partially remedied by some such contrivance as that of Lehmann[*] or of Blondlot,[†] both of whom regulate the current by raising or lowering the zinc by a glass rod working through the cork of the flask. Chittenden and Donaldson [‡] regulate the evolution by the successive use of acids of increasing strength. Both difficulties are, however, obviated by the use of a constant hydrogen generator by which the air of the flask may be swept out and the flow of the hydrogen controlled, thus assuring the uniform rate of deposition of the arsenic, on which the success of the process as a quantitative one largely depends. This idea of a constant generator was apparently first proposed by Verryken,[§] and has been used also in 1888 by Wolff [||] in a modification of Bloxam's electrolytic method.[¶] Any form of generator can of course be used. To the delivery tube is attached a distributing tube, which may be two-way or three-way, according to the number of reduction flasks used. For two flasks an ordinary Y tube suffices, each end of the Y being fitted with a thick rubber connecting tube and a screw clamp, so that the supply of hydrogen may be shut off entirely or controlled for each flask. The reduction flask is a wide-mouthed bottle of about 75 c. c. capacity, fitted with a rubber stopper pierced with three holes. Through one hole passes a right-angled tube reaching to the bottom of the flask, the other end being connected with the distribution tube of the generator. Through the second hole passes the right-angled delivery tube, reaching just below the rubber cork. The third hole serves for the introduction of acid and extract. Through it passes to the bottom of the flask a tube with the bore at the lower end somewhat reduced by melting.[**] In the top of this tube is set a very small funnel.

To the delivery tube of the reduction flask is attached by a rubber stopper a straight bulb drying tube filled with fused calcic chloride (App., 5. *a*), and to the drying tube is connected by a short thick rubber tube the reduction tube, which should be of the hardest and best quality of Bohemian glass (App., 5. *b*), and of as uniform bore as

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[*] Pharm. Zeitschr. f. Russland, 1888, XXVII. 193.

[†] Mémoires de la Soc. Roy. de Sci., Lett. et Arts de Nancy, 1845.

[‡] Loc. cit.

[§] Ref. by Dragendorff, Ermittelung von Giften, 1876, pp. 337 and 317, to Jour. de Pharm. d'Anvers, 1872, pp. 193 and 241.

[||] Fresen. Zeitschr., XXVII. 125.

[¶] Ibid.; also Blyth, loc. cit., p. 533.

[**] That the fluid introduced may not carry any air with it into the flask.

possible, about 7 mm. inside and 8 mm. outside diameter. It should be drawn out before a small blast-lamp flame to as nearly as possible definite bore, which ought to be from 1.5 mm. to 2 mm. at the place of deposition of the arsenic mirror. The finely drawn tube is bent slightly upward, and sealed at the end.

The Reagents (App., 4). — The zinc and sulphuric acid used in the apparatus must be *strictly* free from arsenic, and one should not feel satisfied of their purity unless a stream of hydrogen from the generator, led through the heated tube for several hours, fails to give the slightest deposit. The granulated zinc used in the generator is best of comparatively large size, while that used in the reduction flasks should be quite fine-grained. The acid should have a concentration of one part strong acid (1.82 sp. gr.) to eight parts of water, though a more dilute acid can often be used.

The Course of Analysis. — In the reduction flask is placed a small quantity, not over three grams, of zinc, and the apparatus is connected together. Tightness must be assured, and can be tested for, if the tip of the reduction tube is sealed, by adding through the small funnel a few drops of acid. If these do not fall, the tip of the tube is broken off, leaving an opening of not more than 1 mm. diameter, and then about 20 c. c. of acid are added. The hydrogen is now turned on from the generator, and, after expulsion of the air, lighted, and the flame turned down to a height of 1 to 2 mm. The evolution of hydrogen should be kept at this rate during the reduction of the arsenical solution. Often it is not necessary to use the generator during the reduction, as the evolution from the reduction flask is sufficiently rapid. If it slackens, the generator may be used again, and indeed it is generally necessary to use it toward the close of the reduction. It may happen, on account of too strong acid or increased action after introduction of the extract, that the evolution is too rapid, and the flask becomes heated (App., 5. *c*). To obviate this, the flask may be set in a vessel fitted with an exit tubulus, and filled with cold water, which can be drawn off and replaced when necessary without disturbing the apparatus. An ordinary crystallizing dish with a siphon would answer the purpose.

Shortly after (App., 5. *e*) lighting the hydrogen, the lamp is placed under the heating place and the apparatus tested for absence of arsenic for such length of time as the circumstances direct. In ordinary analyses of wall paper, I allow 15 to 20 minutes' free run before adding the extract.

The lamp should give a large clearly defined flame (App., 5. *f*), and should heat the tube with its oxidizing flame only. An iron cone may be used for increased draught, but not an iron or glass cylinder, for the greater radius of heat given by the latter tends to throw the mirror farther along the tube, and to deposit it irregularly. A convenient rest for the reduction tube is made by soldering three stout copper wires to an old binding screw or post, curving the ends to fit the tube and branching them out, so that the tube lies flat in the curved ends. The binding screw travels vertically on a brass rod melted into a flat, heavy piece of lead, or screwed into the base of an old Bunsen burner.

When the apparatus is found free from arsenic, the extract is added. Previous to this it has been measured or weighed, preferably the latter. The test tube having its weight marked on it, the weight of the extract is quickly determined. Weighings can be made on a balance sensitive to fifty milligrams, which is enough for all practical purposes.

A few drops of the extract are at first added. If no mirror appears in three or four minutes, one eighth to one quarter of the rest may be added, and if in five minutes more there is no mirror, the whole of the extract may be introduced. This cautious addition is necessary in order not to obtain too large a mirror, else a difficulty in estimation might arise, or a new determination might have to be made. A twenty-five minute run is sufficient for the deposition of all the arsenic when the size of the mirror formed in the first fifteen minutes is not larger than that corresponding to 0.05 mgr. of arsenious oxide. If the mirror forming is likely to be larger than this, it is better, after weighing, to start another mirror with another portion of the extract, than to wait for the complete deposition of a mirror which may be too large for comparison with the standards.

The set of standard mirrors is made as follows. One gram of arsenious oxide, purified by repeated sublimation, is dissolved with the aid of a little sodic bicarbonate (free from arsenic), and, after acidification with dilute sulphuric acid, is made up to a litre. Of this standard solution (I.), containing 1 mgr. As_2O_3 to 1 c. c., ten c. c. are taken and made up to a litre, giving the standard solution (II.) containing 0.01 mgr. to 1 c. c. Of this solution, 1 c. c., 2 c. c., 3 c. c., etc., are carefully measured from a burette and introduced into the reduction flask of the apparatus, giving the mirrors corresponding to the same number of hundredth-milligrams. It is necessary to make two or more mirrors of the lower amounts, as, even with careful drawing, the cross sections of the deposition tubes differ, so that the appearance of the mirror from the same amount of arsenic varies, and the variation is more marked as the mirrors decrease in size. Then, for greater convenience in interpolation, mirrors corresponding to the half-hundredths may be made, so that the set which I use contains the following amounts: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, and 0.06. Above 0.06 the difference between the mirrors is so hard to estimate with accuracy, that it is of no advantage to make any above 0.06. Yet in the set which I have photographed, and which is shown in the plate, the following are added for comparison: 0.07, 0.08, 0.09, 0.10.

When the set is not in use, it should be kept in the dark, and at *no* time be exposed to direct sunlight. Although the tubes be sealed, yet there is sufficient air inside to cause a rapid oxidation in direct sunlight, especially with the lower amounts, and a film of arsenious oxide results. By observing this precaution, the set can be kept a long time without alteration.

The readings of the mirrors are far sharper by transmitted than by reflected light, and comparison should always be made by the former. For this purpose I use, at the suggestion of Professor Hill, a small tin box painted black on the inside and outside, and similar in shape and construction to the old-fashioned stereoscopic camera. The height of the box is 20 cm.; width, 7.5 cm.; length at top, 10 cm.; length at bottom, 15 cm. The bottom is open, while the top is covered, and fitted with two eyeholes, 2 cm. in diameter and 4 cm. apart. The set of standard mirrors, as shown in the plate, is mounted, by means of sealing wax, in blackened wooden frames, 18 cm. long by about 7 cm. wide, and 4 to 5 mm. thick. The inner dimensions of the frames are 12 cm. by 4.5 cm. The bottom of the box carries a rabbet of tin, on which the frames may be slid, thus bringing the mirrors under the eyeholes. A second rabbet above the first allows the introduction of a frame carrying the mirror to be compared, which may thus be brought between any two of the standards and compared just as in nesslerization. The box is mounted over a white paper or plate, in front of a good light. The calculation of the amount of arsenic in the area of paper taken follows from the determination of the amount in the aliquot part of the solution. From this can be found the number of milligrams per square meter, which, when multiplied by the factor, 0.0128, gives the number of grains per square yard.

Appendix. — Analytical and Experimental Work.

The experimental work in the investigation of the availability of the method is given in detail in the following pages.

1. *Necessity of Charring.* — Considerable difference of opinion exists as to the necessity for insuring the absence of organic matter in the extract to be tested. Odling,* in 1859, in testing for arsenic in tissues, found that he could obtain arsenic by Reinsch's test in the presence of organic matter, but not by Marsh's. After getting rid of the organic matter by distillation with hydrochloric acid, he had no difficulty with the Marsh test. Blondlot † calls attention to the necessity of completely destroying the organic matter. Chittenden and Donaldson,‡ on the other hand, were able, in the presence of organic matter, to detect very small amounts of arsenic, and consider it of no hindrance. My experience has been, that, while the organic matter may not completely prevent the deposition of small amounts, and is no hindrance in the detection of large amounts, yet the character of the mirror is so altered that comparison with the standards is impossible. Besides, the organic matter causes an increased and irregular flow of gas which tends (App., 5. *f*) to carry undecomposed arseniuretted hydrogen out of the tube. I therefore take the precaution, by thoroughly charring, to insure the absence of organic matter in the extract.

Thoms § digests 100 sq. cm. of the paper on the water bath with (1–7) sulphuric acid, and adds the filtrate directly to the reduction flask. Fleck ‖ considers that digestion with a 25 per cent sulphuric acid is sufficient to extract the arsenic completely, and Reichardt ¶ concurs in this opinion. I cannot agree with this, and consider that the chance of the arsenic being held as arsenious sulphide is alone enough to condemn the method (App., 2. *c*), not to speak of the organic matter extracted.

2. *Use of an Oxidizing Agent in Charring.* — In case the paper contains chlorides, it seemed likely that a portion of the arsenic would be volatilized during the treatment with sulphuric acid. This was

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* Guy's Hospital Reports, V. 367–374.

† Loc. cit. ‡ Loc. cit. § Loc. cit.

‖ Rep. analyt. Chem., 1883, Heft 2.

¶ Archiv d. Pharm., CCXXI. 271.

found to be true to an extent sufficient to warrant the precaution of adding a small quantity of nitric acid to the sulphuric acid, in order to prevent the formation of arsenious chloride.

a. The Presence of Chlorides in Wall Papers. — In order to determine to what extent chlorides exist in wall papers, several analyses were made of papers taken at random. The method was as follows. A measured amount of paper (400 sq. cm.) was thoroughly moistened with a strong solution of potassic nitrate (free from chlorine) on a broad porcelain plate, dried on the plate, and ignited over the plate. The organic matter was practically destroyed. The residue was transferred from the plate to a chlorine free filter, and washed thoroughly with hot water. The filtrate, after acidification with dilute sulphuric acid, was boiled to expel nitrous acid, and, after cooling, titrated according to Volhard with approximately hundredth-normal solutions. There is no danger of volatization of hydrochloric acid even on prolonged boiling, as Gooch and Mar* have shown that a solution containing 0.12 per cent of hydrochloric acid can be boiled down one half without appreciable loss. In titrating, as well as in determining the strength of the standard solutions, it was found that the dilution of the solution affected the end reaction in that the color of the ferric sulpho-cyanate was obscured by that of the argentic chloride, even if the latter were made to "clump together." This difficulty was easily obviated by heating to boiling after adding excess of argentic nitrate, filtering off the chloride, and titrating back in the cooled filtrate. The end reaction was then as sharp as possible.

Analysis of thirteen papers gave an average of 138 milligrams of chlorine per square meter, or 1.38 mgr. in the usual amount (100 sq. cm.) taken for the determination of arsenic. The highest amount was 238 mgr., the lowest 56 mgr. In no case was a paper found free from chlorides.

b. Effect of Chlorides. — A solution of sodic chloride free from arsenic was made up of such strength that 1 c. c. contained 1 mgr. chlorine. Several trials were made of the effect of a known amount of chloride on small amounts of arsenic. 100 sq. cm. S. and S. filter paper (589) were used in each case. After addition of the arsenic and sodic chloride solutions, the paper was dried in the evaporating dish, and the arsenic determined exactly as described, but without using nitric acid. The following table shows the results obtained.

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* Amer. Jour. Science, [3] XXXIX. 293.

Analyses 1–6 were made with duplicate readings which agreed closely.

	Mgr. As_2O_3 taken.	C.c. NaCl, mgr. Cl, taken.	Mgr. As_2O_3 recovered.	Per Cent As_2O_3 recovered.
1	10.0	20.0	5.22	52.2
2	10.0	20.0	4.96	49.6
3	5.0	4.4	3.61	72.2
4	0.5	2.0	0.44	88.0
5	0.1	2.0	0.87	87.0
6	0.05	2.0	0.02	40.0
7	0.01	2.0	0.005	50.0

Analyses 1 and 2 show that the presence of twice the theory of chlorine causes a large loss, with an amount of arsenic comparatively large. Analysis 3 shows a marked loss with less than the theory. Analyses 4 to 7 were made with more chlorine than the average found (1.38 mgr.), but less than the greatest amount (2.38 mgr.); the amounts are respectively 4, 20, 40, and 200 times the theory, and the conditions are more nearly those met with in practice than in analyses 1 to 3. It will readily be seen that the loss is sufficient to warrant the precaution of using an oxidizing agent.

c. Loss by Retention of Arsenic in the Char as Arsenious Sulphide. — The presence of the sulphide in papers is not very common. Yet papers colored with ultramarine occur frequently, and the sulphuretted hydrogen set free from this by the sulphuric acid acts on the arsenic compound, and thus a large part of the arsenic remains in the char as the sulphide, insoluble in dilute sulphuric acid. The following analyses of a paper are sufficient to show the danger of loss from this source. The paper had a light blue ground, and the odor of sulphuretted hydrogen was apparent on addition of sulphuric acid. 100 sq. cm. charred with sulphuric acid and a few drops of nitric acid gave an amount of arsenic corresponding to 5.9 mgr. per square meter. 100 sq. cm. charred with sulphuric acid alone gave 4.5 mgr. per square meter. The char was then extracted with ammonia, and the extract evaporated with sulphuric acid and a drop of nitric acid. This yielded 0.01 mgr., corresponding to 1 mgr. per square meter and bringing the total amount up to 5.5 mgr., which agrees with the first analysis.

d. The Deposition of Arsenic from a Solution of Arsenic Acid. — The question arises whether the conversion of the arsenious to arsenic acid by use of an oxidizing agent would cause the arsenic to be held back. This was quickly determined by comparison of the standard mirrors with a set prepared from a solution of arsenic acid, of which

1 c. c. contained 0.01 mgr. As_2O_3, as As_2O_5. The mirrors agreed sharply. This is at variance with the results of Headden and Sadler,* who found, in using the method of Chittenden and Donaldson, that it was necessary to subject the arsenic acid to preliminary reduction in order to obtain all the arsenic present. The reason for this is, probably, that a very small quantity of arsenic acid, such as would occur under the conditions of this method, is more quickly reduced by nascent hydrogen, while the comparatively large quantity used by Headden and Sadler would take more time. They do not show that prolonged treatment in the Marsh reduction flask would not have eliminated this error.

e. The Use of Nitric Acid as an Oxidizer. — Nitric acid suggests itself at once as the most convenient oxidizing agent. In this connection may be mentioned the method proposed by Blyth,† which consists in soaking the paper in potassic chlorate, drying, burning, and extracting with water. Hager ‡ substitutes sodic nitrate for the potassic chlorate. Many destroy the organic matter by hydrochloric acid and potassic chlorate, as in the case of tissues. Lyttkens § uses sulphuric acid and potassic chlorate, and Lenz,‖ commenting on this, considers it the best means of treatment of the paper. The German law ¶ of 1888 prescribes the treatment of fabrics with strong hydrochloric acid and distillation with ferrous chloride. None of these methods in the analysis of wall papers and fabrics have any advantage over charring with the simple addition of nitric acid, and all require more time.

That all the arsenic may be recovered when nitric acid is used is shown by the following: 0.01 mgr. arsenious oxide was added to 100 sq. cm. of filter paper and a drop of strong nitric acid added before charring. The mirror obtained corresponded to 0.01 mgr.

1 mgr. As_2O_3 and 5 cc. sodic chloride solution (5 mgr. chlorine) were added to 100 sq. cm. filter paper and treated with a mixture of one part nitric to six parts sulphuric acid. Duplicate readings gave 1.095 mgr recovered, an error no greater than that which might occur from the method.

10 mgr As_2O_3, as As_2O_5, were added to 100 sq. cm. filter paper, and

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* Amer. Chem. Journal, VII. 338; Ber. d. deutsch. Chem. Gesell., XIX. 116.

† Loc. cit., p. 532.

‡ Pharm. Centralhalle, XIII. 145.

§ Ref. Fres. Zeitschr., XXII. 147, from Landw. Versuchsstat., XXVI. 305.

‖ Fres. Zeitschr., XXII. 147.

¶ Ibid., XXVII. 471.

treated with sulphuric acid alone. Duplicate readings gave 9.94 mgr. recovered.

Finally, 100 sq. cm. of a wall paper containing no arsenic was, after addition of varying amounts of As_2O_3, charred with a nitrosulphuric acid containing one part nitric to thirty of sulphuric acid. The following table shows the results of four analyses. The readings on 2, 3, and 4 were in duplicate.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 found.	Mgr. per Sq. Meter taken.	Mgr. per Sq. Meter found.
1 . . .	0.01	0.009	1.0	0.90
2 . . .	0.10	0.0995	10.0	9.95
3 . . .	1.00	0.977	100.0	97.70
4 . . .	10.00	10.30	1000.0	1030.00

f. Effect of Free Nitric Acid in the Reduction Flask. — Rieckher[*] does not consider the presence of free nitric acid to be detrimental, while Fresenius[†] takes the opposite ground. Blondlot[‡] thinks that free nitric acid gives rise to the formation of a solid hydride of arsenic on the zinc, thus causing the retention of part of the arsenic. Without discussing the correctness of this statement, which seems to have been quite universally accepted, we have only to consider the effect of a trace of the acid on the deposition of the mirror, as the method of charring would leave, at most, but a very small amount of free nitric acid in the extract. 0.02 mgr. and 0.05 mgr. As_2O_3 were added to the reduction flasks in which were about 20 c. c. dilute sulphuric acid, and immediately afterward a drop of strong nitric acid was added to each. The dilution was considerable, but not so great as might occur in practice. The mirrors were clearly defined, and corresponded sharply to 0.02 mgr. and 0.05 mgr. respectively.

3. *Extraction of the "Char."* — It is necessary that the char should be thoroughly pulverized and extracted with *hot* water. Considerable loss is likely to occur if these precautions are disregarded, as the following results show: —

To 100 sq. cm. of a wall paper free from arsenic, 1 mgr. As_2O_3 was added, and the char was extracted with 30 c. c. cold water. 0.77 mgr. were recovered, = 77 per cent.

To the same amount of paper 5 mgr. were added, and the char extracted with 30 c. c. cold water. 3.82 mgr. were recovered, = 76.4 per cent.

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[*] Neues Jahrb. f. Pharm., XX. 3.

[†] Fres. Zeitschr., II. 389.

[‡] Comptes Rendus, LVII. 596.

To the same amount of paper 10 mgr. were added, and the char extracted as before, but, in addition, the particles were well triturated. 9.19 mgr. were recovered, = 91.9 per cent.

That this loss was not due to error in estimation of the mirrors was shown by repetition of the first two trials, mirrors being obtained from separate portions of the same extract. The char was triturated in each case: —

1 mgr. As_2O_3 gave 0.9 mgr. and 0.9 mgr. Average, 90%.
5 " " " 2.92 " " 2.95 " " 58.60%.

That arsenic would be left in the char was shown as follows: 100 sq. cm. of paper as above, after addition of 5 mgr. As_2O_3, were charred, and the finely ground mass extracted first with cold water. 3.11 mgr. were recovered, = 62.2%. The residue was then extracted with 30 c. c. hot water. 1.63 mgr. were recovered, = 32.6%. A third extraction with hot water gave a solution free from arsenic. Total amount recovered, = 4.74 mgr. = 94.8%.

The quality of the paper has no effect on the loss: 5 mgr. As_2O_3 were added to 100 sq. cm. filter paper and treated as before. Two readings from the same cold extract gave 3.51 and 3.46 mgr. respectively. Average, 69.9%. Finally, to show the practical completeness of extraction with only 25 to 30 c. c. hot water, 100 sq. cm. of filter paper were charred with different amounts of arsenious oxide.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 recovered.				Per Cent As_2O_3 recovered.
		Extract 1st.	2d.	3d.	Total.	
1 . . .	5.0	4 99	0.08	0.0	5 07	101.4
2 . . .	5.0	4.98	0.07	0.0	5.05	101 0
3 . . .	10.1	10 65	0.06	0.0	10.71	106 7
4 . . .	10.0	10.37	0.0	—	10.37	103.7

10 mgr. of arsenious oxide per 100 sq. cm. of paper would correspond to 1,000 mgr. per sq. meter, which is an unusual amount. Hence any smaller amounts would be easily extracted. It should be borne in mind that the error is necessarily great in such large amounts, for the deposit which is compared with the standards is so small a proportion of the total amount that a slight difference in reading is proportionally increased.

4. *Reagents.* — Many chemists prefer to use hydrochloric acid instead of sulphuric acid, on account of the quicker action of the former on the zinc. Opinions vary considerably as to the error arising from volatization of zincic chloride, and consequent deposition at the heating

place, when hydrochloric acid is used. Liebig,* very soon after the publication of Marsh's method, called attention to possible error from this source, and several years later Wackenroder† confirmed Liebig's opinion. Beckurts ‡ claims that there is no danger to be feared, but does not show conclusively that this is the case. Brescius § recognizes the chance of error, and recommends passing the gas through sulphuric acid, if hydrochloric acid is used for generation. The committee of the British Health Association, above referred to, recommends the use of hydrochloric acid, without comment on its possible disadvantage.

While the volatilization of zincic chloride might not interfere with the detection of arsenic in considerable quantity, yet it is of primary importance in this method for the mirror to be of arsenic alone, and hence capable of comparison with standards. We cannot, therefore, run the risk of the small mirror being contaminated by any impurity whatever. For this reason, if for no other, the use of hydrochloric acid is wholly unadvisable. Then the time gained in using hydrochloric acid is not to be considered in this method, as the use of a constant generator reduces the time of analysis so decidedly.

The same desire to hasten the evolution of hydrogen in the ordinary Marsh process has led to the addition of stimulants to the action in the shape of platinic chloride or cupric sulphate. Bernstein ‖ has shown that the use of platinic chloride is inadmissible, because arsenic is thereby held back. At the same time, however, he finds no loss when the zinc is platinized or silvered before being used. Headden and Sadler ¶ agree with Bernstein in the case of platinic chloride, and find that cupric sulphate also causes a loss. They also get low results by using a spiral of platinum wire in contact with the zinc. Here, again, the use of the constant generator precludes the necessity for increasing the sensitiveness of the zinc.

Mohr,** in 1837, called attention to the fact that the residual zinc even after careful washing contained arsenic. This would seem to substantiate the statement of Blondlot, quoted above, concerning the solid hydride of arsenic. Fresenius †† also considers that the effect of nitric acid is due to the formation of a hydride. When we consider the case of the mere detection of arsenic by the Marsh process, where all the arsenic is not necessarily reduced to arseniuretted hydrogen, it

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* Ann. d. Chem. u. Pharm., XXIII. 217.

† Archiv f. Pharm., LXX. 14.

‡ Ibid., CCXXII. 653.

§ Dingl. Polyt. Jour., CLXXXVI. 226.

‖ Inaug. Dissertation, Rostock, 1870.

¶ Loc. cit.

** Ann. d. Pharm., XXIII. 217.

†† Loc. cit.

is quite possible that part is left in the zinc, especially if the extract be not free from nitric acid. But in this method, where all of a very small amount of arsenic is to be reduced, and the action is pushed as far as possible, the probability is that no arsenic is left in the zinc. I have often, after deposition of the mirror, pushed the action as far as the complete solution of the zinc, and have never observed any increase of the mirror at the close. It would seem hardly possible for the solid hydride to remain in that state in a reducing medium for such a length of time (compare also 2. *f*). A large amount of carbon in the zinc is apt to cause too rapid evolution, but I cannot confirm the statement of Headden and Sadler * that zinc containing carbon causes a loss of arsenic, and that the zinc must in consequence be free from carbon.

5. *General Precautions.* — *a. Means of drying the Hydrogen.* — The use of sulphuric acid is not allowable. I have found the statement of Dragendorff † to be true, that sulphuric acid absorbs arseniuretted hydrogen. This is assumed by Janowsky ‡ to be due to decomposition into arsenic and hydrogen, but no proof is given. Dragendorff † quotes the suggestion of Otto,§ that a small amount of fused potassic hydroxide be placed before the fused calcic chloride, in order to absorb any sulphuric acid which might be carried over, it being possible that the acid might act on the calcic chloride, giving hydrochloric acid, which might form arsenious chloride and thus cause loss of arsenic. The potassic hydroxide would also hold back sulphuretted hydrogen. It is well known that potassic hydroxide absorbs antimoniuretted hydrogen, and it has been recently shown by Kuhn and Saeger,‖ as well as by Headden and Sadler,* that arseniuretted hydrogen is also absorbed by it. There is, however, no need of its use as a precaution against either of the contingencies mentioned above.

Lyttkens¶ considers sulphuric acid to be a better drying agent than calcic chloride, and Lenz ** agrees with him, but neither shows that there is no loss of arsenic attending its use.

As to Headden and Sadler's * statement, unsupported by analysis of the calcic chloride used, that fused calcic chloride holds back arsenic when moist, I have never met with any indication that there was danger of loss from this source.

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* Loc. cit.

† Ermittelung von Giften, 2te Aufl., p. 336.

‡ Ber. d. deutsch. chem. Gesell., VI. 216.

§ Ausmittelung der Gifte.

‖ Loc. cit.

¶ Loc. cit.

** Loc. cit.

b. Impurities in the Glass of the Deposition Tube. — The errors resulting from the presence of lead and arsenic in glass have been frequently mentioned. The presence of lead in any hard glass fit for use is scarcely probable. The formation of a mirror from either of these sources would however be detected at the start, and the glass rejected at once. I have not found any case of error attributable to impurities in the glass.

c. Temperature of the Reduction Flask. — Dragendorff[*] quotes Kolbe[†] as having shown that sulphuretted hydrogen is always formed by the action of sulphuric acid on zinc, if the reaction temperature exceeds 30°, and recommends on this account that the flask be cooled. The quotation is misleading. What Kolbe showed, and Fordos and Gélis[‡] called attention to the same point some time before Kolbe, was, that if strong acid be added to the flask to increase the action, there was reduction of the acid at the temperature mentioned. With acid diluted with two parts of water no reduction took place. As one would hardly add strong acid to the flask, the danger of formation of sulphuretted hydrogen from mere action of the acid on the zinc is not to be feared. Yet it is necessary to keep the flask cool in some such manner as suggested, if only to prevent too violent action of the acid which may occur from accidental presence of organic matter.

d. Necessity of boiling the Char with Water. — The formation of a "sulphur mirror" is often met with, due to the decomposition of sulphuretted hydrogen at the heating place. Then, too, Brunn[§] has lately shown that sulphuretted hydrogen and arseniuretted hydrogen form, when heated, hydrogen and arsenious sulphide. The necessity of boiling the char with water is therefore evident, in order that no sulphur dioxide be left in the extract to be reduced by the nascent hydrogen.

e. Beginning of Heating. — If the tube be heated as soon as the hydrogen is lighted, the small amount of oxygen left in the flask causes the formation of water in the deposition tube. This can be avoided, if desired, by waiting a few minutes before setting the lamp under the tube.

f. Rapidity of Gas flow and Amount of Heat. — In the method of Chittenden and Donaldson it is necessary to guard against too rapid evolution of gas, and the heating surface must be very great in order

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[*] Loc. cit., p. 336.

[†] Ann. d. Chem. u. Pharm., CXIX. 174.

[‡] Comptes Rendus, XIII. 437.

[§] Ber. d. deutsch. chem. Gesell., XXII. 3202.

that no arseniuretted hydrogen shall escape decomposition. In this method, the amount of heating surface need not be greater than that given by a good burner, and I have assured myself by direct experiment that no arsenic escapes under the ordinary conditions when the size of the mirror is not above 0.06 mgr. It is necessary, however, for the stream of gas to be slow and regular. Hence the disadvantage of organic matter in the extract, causing an increased and irregular flow of gas.

6. The following table contains some analyses, taken at random, illustrative of the method.

	Sq. Cm taken.	Grams Extract.	Gr. Extract taken.	Mirror obtained Mgr. As_2O_3.	Mgr. As_2O_3 found.	Mgr. As_2O_3 found per Sq. Meter.
1 . .	100	33.17	33.17	0.030	0.030	3.0
2 . .	100	32.27	6.00	0.017	0.094	9.4
			5.81	0.015	0.083	8.3
3 . .	100	31.84	5.66	0.045	0.253	25.3
			1.90	0.015	0.251	25.1
4 . .	25	29.69	2.64	0.016	0.179	71.9
			2.65	0.017	0.191	76.2
5 . .	111.15	33.66	0.78	0.035	1.510	136.0
			0.46	0.020	1.460	132.0
6 . .	25	30.67	1.01	0.040	1.214	485.6
			2.08	0.080	1.180	472.0
7 . .	12	28.83	0.48	0.030	1.802	1502 0
			0.61	0.043	2.032	1693.0

7. *Comparison of Results obtained by the Berzelius-Marsh Process with those obtained by other Methods of Analysis.* — In order to test the availability of the process, it became necessary to analyze, by one of the general quantitative methods, some of the papers which had been analyzed by the Berzelius-Marsh method. In the analyses given below, the eventual determination was made by an approximately hundredth normal solution of iodine, and, when necessary, titrating back with a sodic thiosulphate solution of corresponding strength. I find a similar method to have been proposed some time ago by Holthof.* Considerable difficulty was met with at first in finding a suitable method of getting the arsenic from the paper into proper state for titration. A measured piece of paper (100–400 sq. cm.) was treated on a porcelain plate with a strong solution of

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* Fresen. Zeitschr., XXIII. 378.

potassic nitrate, dried on the plate, burned over the plate, and the residue washed off into an evaporating dish. The residue was then treated with about 5 c. c. strong sulphuric acid and evaporated until sulphuric acid fumes appeared. To insure the complete expulsion of nitric and nitrous acids, the mass was boiled down again, after addition of a little water. It was then taken up with hot water, filtered, and washed with hot water. The filtrate was kept at 60–70° for half an hour, and sulphur dioxide passed through. After boiling the reduced solution in the flask until sulphur dioxide was expelled, it was made alkaline with sodic bicarbonate, cooled, and titrated. The results obtained were far from satisfactory, but the analyses agreed closely in three cases, which are given below. (Papers numbered 111, 395, and 42 in final table.)

Next, instead of ignition with potassic nitrate, the paper was treated exactly as in the Berzelius-Marsh method, with nitrosulphuric acid (1–30), taking care to get rid of all nitric and nitrous acids. The extract was reduced at 60–70° by sulphur dioxide, the excess of the latter driven off by boiling, and the cooled solution made alkaline with sodic bicarbonate, and titrated. In one case the arsenic was precipitated from the extract by sulphuretted hydrogen, and the arsenious sulphide converted to arsenious acid, and titrated. The amount of time required for this, however, offset any advantage from it. Although by care this method can be employed, yet the details require much time and the chances for error are many. Duplicate analyses agreed closely in two cases which are given below. (Papers numbered 194 and 155 in final table).

The method finally used was adapted from the well known process of Schneider* and Fyfe.† A measured quantity of paper was cut into small pieces and placed in a 500 c. c. distilling flask connected with a cooler. Attached to the latter was a receiver with a second tubulus carrying a long tube which served as an air cooler. About 100 c. c. of hydrochloric acid, diluted one half, were added to the flask, and the mixture distilled, slowly, almost to dryness. It was found by trial, that in nearly every case all the arsenic came over in one distillation, and, if not, that a mere trace was left in the residue. The distillate was transferred to a flask, potassic chlorate added, the solution boiled down one half, transferred to an evaporating dish, and evaporated to dryness, with the addition of a few drops of strong sulphuric acid. The residue was generally white. If dark, from pres-

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* Jahrb. d. Chem., 1851, p. 630.

† Jour. f. prakt. Chem., LV. 103.

ence of volatile organic matter not destroyed by the potassic chlorate, the addition of a few drops of strong nitric acid and evaporation expelled the organic matter. The residue was then washed into a flask with about 50 c. c. water, and reduced and titrated as in the previous cases.

The method was tested by the following analyses of filter paper to which known amounts of arsenic were added, 200 sq. cm. of paper being used in each case.

	Mgr. As_2O_3 taken.	C.c. Iodine used. 1 c.c. = 0.9815 mgr. As_2O_3.	Mgr. As_2O_3 found.	Per Cent As_2O_3 found.
1 *a* . . .	5	5.1	5.01	102.1
1 *b* . . .	5	5.3	5.20	
2 *a* . . .	5	5.0	4.91	100.1
2 *b* . . .	5	5.2	5.10	
3 *a* . . .	25	25.1	24.64	98.4
3 *b* . . .	25	25.0	24.54	

The residues from the distillations in the last analyses were, after the addition of a few drops of nitric acid, charred with sulphuric acid and "marshed," giving mirrors corresponding to 0.015 mgr. and 0.02 mgr. respectively, showing that a mere trace was left in the flasks.

The following papers were analyzed by this method.

Number of Paper.	Sq. Cm. taken.	C.c. Iodine used. 1 c.c. = 0.9815 Mgr. As_2O_3.	Mgr. As_2O_3 found per Sq. Meter.
194 . . .	200	17.20	844.00
194 . . .	200	17.30	849.00
406 . . .	400	3.10	76.07
406 . . .	400	3.00	73.61
39 . . .	400	2.80	68.71
39 . . .	400	2.70	66.25
392 . . .	380	1.80	46.50
393 . . .	400	0.38	9.33
393 . . .	400	0.36	8.83
359 . . .	400	1.30	31.90
359 . . .	400	1.10	27.00

Finally, the following table shows the comparison of the results obtained by the volumetric method with those obtained on the same papers by the Berzelius-Marsh method. The first two columns compare the results in milligrams per square meter, and the second two in grains per square yard. Each result is the mean of two, unless specified.

Number of Paper.	Mgr. As_2O_3 per Sq. Meter.		Grains per Sq. Yard.	
	Berz. Marsh.	Volumetric.	Berz. Marsh.	Volumetric.
393	8.8	9.1	0.11	0.12
359	24.0	29.5	0.31	0.38
392	46.8	46.5 *	0.60	0.60 *
39	64.9	67.5	0.83	0.86
406	72.8	74.9	0.94	0.96
114	110.4	108.7	1.42	1.39
395 ‡	193.0	210.4	2.47	2.69
42	478.8	421.8	6.13	5.40
194	842.0	832.7 †	10.78	10.66 †
155	1527.1	1478.5	19.55	18.93

* One determination, † Four determinations. ‡ 395 was a piece of "Turkey red" cloth.

Before the above described method was worked out, it was thought that it would give merely an approximation of the amount of arsenic in wall papers and fabrics, which would allow one, for instance, to pass judgment on the articles from a sanitary standpoint. Not only, as will be seen from the table, does the method give an approximation to the actual amount when ordinarily conducted, but with care it can be made to give results worthy of comparison with other quantitative methods. The greatest error occurs naturally in the estimation of large amounts, but in this case an approximation would answer until a more exact determination was called for.

The process will, I think, be also found of great value in toxicological work, not only as a rapid means of determining the quantity of arsenic present, and as a check on other methods, but also as the only means of accurately determining the amount when the arsenic is present in minute quantity. In such work the organic matter would not generally be charred, but the arsenic would be extracted by the method of distillation. I hope to investigate the extension of the method to toxicological work.

The limit of arsenic that I have been able to detect with certainty by the Berzelius-Marsh method is 0.001 mgr. As_2O_3 or 0.0007 mgr. As. I shall not here take up the much discussed question of the delicacy of this as compared with other methods, but I think it will be agreed that no other method enables one to determine quantitatively such small amounts.

In conclusion, I have to thank my assistant, Mr. Charles Walker, very sincerely for his valuable services in most of the analytical work of this paper.

UNITED STATES NAVAL ACADEMY, ANNAPOLIS, MD.,
February, 1891.

V.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY.

XV.—ON THE STRUCTURE AND DEVELOPMENT OF CHOREOCOLAX POLYSIPHONIÆ, Reinsch.

By Herbert Maule Richards.

Presented by W. G. Farlow, May 12, 1891.

Heretofore comparatively little has been known concerning the obscure parasitic alga, *Choreocolax Polysiphoniæ,* Reinsch. Little has been written concerning it, and, so far as I know, only one other of the various forms included in the original description under the same genus has been the subject of even a note. It was with a hope of adding something new to our knowledge of it that I undertook the examination of this plant. The observations resulted in the discovery of several interesting facts, which, together with a general description of the alga are embodied in this paper.

The literature concerning the genus Choreocolax, besides the original description, consists of only a few scattered notes. The genus was first described and figured by Reinsch in his "Contributiones ad Algologiam et Fungologiam."[*] There he mentions several species parasitic on various algæ, but described only from sterile specimens. Among them is *Choreocolax Polysiphoniæ,* growing on *Polysiphonia fastigiata,* the only species that has been reported to have been found on the American coast since Reinsch's original descriptions. The next notice of these parasites is by Farlow, in his New England Algæ,[†] where in a foot-note he briefly mentions them. In a paper published later,[‡] he makes mention of *C. polysiphoniæ,* describing for the first time the tetraspores of this plant. They develop from the terminal cells of the plant, and may be either tripartite or cruciate ; usually the

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[*] Page 61, Plate XLIX.

[†] Page 101.

[‡] On some New or imperfectly known Algæ of the United States. Bull. Torrey Bot. Club, Vol. XVI. No. 1, p. 6, Plate LXXXVII.

latter. Recently Reinke and Schmitz found in one of the species formerly described as *C. mirabilis* cystocarpic fruit which enabled them to ascertain its true affinities. They placed it among the Gelidiaceæ, and gave to it the new generic name of Harveyella.* Their reasons for placing it in a new genus were twofold. They rightly thought *C. mirabilis* to be widely different from *C. Polysiphoniæ*. Besides this, *C. Polysiphoniæ* was described before *C. mirabilis* in Reinsch's original account, so that the former is to be regarded as the type of the genus Choreocolax rather than the latter. Besides these notes, Choreocolax and Harveyella are scarcely more than mentioned by name in a few other places. Schmitz in his arrangement of the genera of the Florideæ † places them both among the Gelidiaceæ. Batters mentions them also in his List of Berwick Algæ, ‡ and reports the collection of tetrasporic specimens of *C. Polysiphoniæ*, but has nothing new to add regarding them. Thus it will be seen that the literature concerning these interesting parasites is very scanty.

Choreocolax Polysiphoniæ grows, as has been already stated, upon *Polysiphonia fastigiata*, a common alga along the Northern New England coast. The parasite was sufficiently abundant at Nahant, Mass., to be collected in considerable quantities from the middle of November to the latter part of the following March. I found it also at Newport, R. I., growing on the Polysiphonia, on the more exposed points. *C. Polysiphoniæ* has been collected by Dr. W. A. Setchell at various points along Long Island Sound, though its host is much less common there than farther north. Mr. F. S. Collins has sent me specimens he found at Mount Desert, on the Maine coast, during the month of July, 1890. From all reports, however, it is found nowhere in such quantities as at Nahant. Batters § mentions *C. Polysiphoniæ* as having been collected on the British coast at Berwick Bay, but adds that it is rare. The distribution of this alga, then, is fairly wide, and it is probable that wherever its host is found it may also be expected in greater or less quantities.

To the naked eye the fronds of Choreocolax appear as small whitish brown dots of variable size, situated almost always in the dichotomies of the Polysiphonia. In some specimens collected at Nahant, almost every axil except the ones of the very youngest branches was

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* Algenflora der west. Ostsee. Deutsch. Anth., Kiel, 1889, p. 28.

† Systemat. Uebersicht der bisher bekannten Gatt. der Florideen. Flora, 1889, Heft V p. 439.

‡ Pages 126 and 142.

§ List of Berwick Algæ, p. 142.

occupied by a frond of the parasite. Such cases as these, however, are not usual; ordinarily the host is not so completely covered with the Choreocolax. That the parasite has a deleterious effect on the Polysiphonia is very evident, for the fronds of the latter, on which the Choreocolax is most plentiful, are always paler and less vigorous-looking than the fronds not so affected. The growing tips of the host plant, which usually give every appearance of active growth, are fewer in number, small, and often distorted. Often the terminal branches can be seen to have shrivelled up and rotted away, probably from insufficient nourishment. In fronds of Polysiphonia, all stages of this decay may be seen, which varies in intensity according to the amount of Choreocolax on the frond. Some exceptionally strong plants seemed little affected, though considerably attacked by the parasite.

On examining specimens of *Choreocolax Polysiphoniæ* with a hand lens, they are seen to be usually light-colored masses varying in shape from a flattened hemisphere to almost a sphere. The surface of most of them is smooth and the outline of the frond is regular (Fig. 1), though some are divided unevenly into several lobes (Fig. 2). The cause of this latter condition will be discussed subsequently. The size of these masses that constitute the external portion of the Choreocolax is very variable, ranging from small spots that can scarcely be seen, even with a powerful hand lens, to bodies about 2 mm. in diameter. The majority of them, however, are not over 1.5 mm. in diameter. The small fronds are flattened, becoming more and more nearly spherical as they increase in size and age. It is only the large fronds that are lobed in the manner mentioned, the small ones are always quite regular in shape. The color of the fronds varies from the translucent whitish color of the young ones, to the dirty reddish appearance of the adult specimens. Occasionally the latter are dark brownish red, though usually they are not very deeply colored, and may sometimes be almost as white as the young fronds. The larger masses of *C. Polysiphoniæ* are of a tough cartilaginous consistency, firmer and more unyielding than the more gelatinous younger fronds. The appearance of *C. Polysiphoniæ* is so unique, that, together with its habitat, the collector is easily informed of the identity of this rather insignificant-looking alga.

Before describing the growth and development of the frond, it will be best to explain the structure of the adult plant, which cannot be well compared with the conditions presented by other algæ. A section through the frond shows it to be composed for the most part of large, somewhat irregular cells, approaching a spherical or cylindrical shape, which are filled with coarsely granular, almost colorless contents. The cells are separated, except at narrow points of contact, by an almost structureless gelatinous intercellular substance (Fig. 8). This gelatinous substance, which contains a large amount of water, is found to a greater or less extent between all the cells of the frond, and gives to it the consistency already mentioned. The large cells which make up the interior of the frond are not at all regular in either size or shape, some departing so far from the spherical as to become almost branched, by the excessive growth of some portion of the cell in some other direction than that of the main axis. They are not arranged in filaments, or in any distinct order, but are joined in a loose parenchymatous network. In the parts of the frond near its point of attachment to the host plant, the cells are seen to be smaller and of a different shape than those of the rest of the plant. They are cylindrical, with one axis considerably longer than the others, and are arranged in filaments of greater or less length (Figs. 8, 14). The filaments which may or may not branch, make their way beneath the peripheral siphons of the Polysiphonia, encircling its axial row of cells. Usually these filaments extend from the frond of Choreocolax from which they arise, through the length of three or four cells; cases were observed, however, where they had penetrated as many as ten cells from their starting point. It is by means of these cells that the Choreocolax obtains elaborated material from the Polysiphonia, on which it depends, in a large measure at least, for its nourishment. The close connection which the filamentous cells of the parasite have with the cells of the host may be easily demonstrated. A section shrunk in glycerine and stained with Hofmann's blue, enables one to see with the greatest distinctness threads of protoplasm connecting the cells of the two plants (Fig. 7). Material killed in osmic acid also shows this point to advantage. At the same time it will be seen that the cells of the Choreocolax attach themselves almost wholly to the cells of the central siphon, although sometimes the walls of the peripheral siphon are penetrated and the material afforded by them appropriated by the parasite. *C. Polysiphoniæ* is then, as Reinsch first maintained, a true vegetable parasite, which depends in the main for its nourishment on the materials provided by its host, exerting upon the latter nothing but a deleterious influence. These filaments were never seen to connect with any of the external swellings except the one from which they arose. Each swelling then represents a separate frond, and there is no continuous growth of filaments which ramify through the host, rising at places in external prominences for the purpose of producing fruit. In the external portion of the frond, the proportion of the filamentous cells to the globose ones is very variable. Sometimes the former encroach far on the latter, while again the globose cells may entirely exclude the filamentous ones from the external frond. In the same way, the size of both kinds of cells varies a great deal ; in fact, in all the structures of the frond, even in rare cases in the fruit, a great diversity in appearance may be noticed.

Besides the kinds of cells already described, the peripheral cells of the frond present a very characteristic appearance. Nearer the outside the cells are seen to be smaller, more nearly spherical in shape, and more regularly arranged, than in the rest of the frond. The gelatinous intercellular substance is also considerably diminished in quantity in this region. Those cells which form the extreme outer layer are still different in shape from any of the others. They are somewhat elongated and pyriform, the smaller ends being directed inwards (Figs. 5, 8). They constitute the growing part of the frond, as will be described later, in discussing the development of the plant. The contents of these outer cells is more granular than that of the others, and the nuclei are more distinct ; in fact, they present all the appearances characteristic of growing cells. Directly outside of the pyriform cells there is a thick sheath of cellulose, which covers and protects the whole frond (Figs. 8, 17). This outer skin of cellulose is not formed by the fusion of the exterior walls of the peripheral cells ; they are only loosely connected with it, and may be detached from it without injury. The cellulose sheath may be dissected off in large pieces, when it is seen to be almost structureless, except for the depressions left by the cells which had formerly been attached to it, and for the irregular blotches of brownish red coloring matter in it. By this means the pigment to which the color of *C. Polysiphoniæ* is due may be seen to be contained almost entirely in this external covering. Sometimes the peripheral cells may be also tinged with brown, while in one or two cases the whole tissue of the frond partook of this color. The sheath is nothing more than a thickening of the gelatinous intercellular substance on the outside of the frond. This gelatinous substance is itself but a modification of a portion of the walls of the cells, and gives a cellulose test with chloriodide of zinc as well as the sheath. As in the case of the other cells of the frond, those near the periphery are subject to some variation. In those fronds where the filamentous cells extend into the external protuberance of the frond, the peripheral cells partake more or less of the same character. One extremely exaggerated case was noticed, in which the cells around the circumference of the frond were enormously elongated. This frond happened to be tetrasporic, and the tetraspores were also greatly elongated and deformed. The contents of the cells present little of interest. The outer cells are filled with a very highly granular protoplasm, in which the nucleus is very conspicuous. The inner ones contain less of the granular protoplasm, and the nucleus is rather more indistinct. All the cells of the plant are usually colorless, though sometimes they may be tinged with purple, especially the filamentous ones in closest contact with the Polysiphonia. Of ordinary starch there is no trace to be found, iodine giving only a deep brown color to the whole of the contents of the cells. The walls of the cells are cellulose, and are not remarkable. One interesting feature regarding the cells of *C. Polysiphoniæ* is their great variability in the amount of contained food material. This varies from the condition found in the globose cells of the young plant, which are gorged with protoplasm, to the decidedly contracted and starved appearance presented by the cells of some of the adult plants. This latter condition is particularly to be noticed in the tetrasporic fronds which are almost ripe, the growth of the tetraspores having apparently taken all the food material held in reserve by the plant. Figure 8 shows a tetrasporic frond where the cells are somewhat affected, and is a good example of the condition of the average frond. In Figure 14 the cells are seen to be well gorged. The difference in appearance is often so striking as to lead one to think at first sight that plants are not of the same species.

The development of the frond I was able to follow with considerable certainty, except in the youngest stages, of which fewer specimens were found. As has been said before, the fronds of *C. Polysiphoniæ* are almost always found in the dichotomies of the host plant, and the reason for this can be explained by the following circumstances. In the axils of the branches of *Polysiphonia fastigiata* there is often collected more or less organic or inorganic material, and they are also frequently occupied by some of the many epiphytic algæ that grow upon this plant. Besides the natural shelter afforded by the axils, these growths enable the spores to become attached before they are able to make their way through the tissues of their natural host. The spore becomes buried in the organic matter collected in the axil, and in this position begins to germinate. The earliest stage of a developing spore of Choreocolax that was found was one where five cells were to be distinguished. The spore had apparently divided into four parts, and then after some growth one of these four cells had divided again into two, — a process which the other cells were probably about to undergo. There is little to be said regarding this; what nourishment the young frond required to carry on the growth was probably taken from the organic material in which it was buried. No growth had yet penetrated the cells of the Polysiphonia.

The next stage that was observed in the development of the frond was rather more complicated. The young frond was here composed of a considerable number of cells, which, however, presented as yet no very definite arrangement (Fig. 3). The gelatinous intercellular substance was present to some extent, and a tougher layer of it already covered the outside surface. The first indications of the growth of the parasite into the Polysiphonia were also seen here. In the figure (Fig. 3) where this stage is shown, two cells will be seen that have thrust themselves between the cells of the host plant, and have grown some little distance inwards. Even as early as this the young frond of Choreocolax must have obtained some nourishment from the Polysiphonia, or it would not have given evidence of so much activity of growth. Other than this there is no differentiation in the cells of the frond; the characteristic arrangement of the terminal layer that is developed in the adult frond has not yet made its appearance. Having once forced their way into the tissue of the Polysiphonia, the cells of the Choreocolax grow more rapidly, and finally come to encircle cells of the host plant. New filaments push their way in, and grow in both directions, between the central and peripheral siphons of the Polysiphonia, attaching themselves chiefly to the former.

In the mean time the external portion of the frond has been increasing in size. The cells which have pushed themselves into the host plant have, besides fastening themselves to its cells, begun to send out branches upwards, which, by subsequent growth, are to form a part of the external protuberance of the frond. As these cells increase in number they press outwards, and, joining with the rapidly developing external portion already formed, displace the cells of the host plant in the immediate neighborhood of this growth. Later, the displaced cells of the Polysiphonia are entirely enveloped by the growing Choreocolax. No morbid growth is stimulated in them, however; they remain entirely passive, and are gradually absorbed by the parasite, so that in adult specimens there is usually no trace of them left.

Comparatively early in the development of the frond, before the internal growth of the vegetative filaments has pushed aside the cells of the Polysiphonia to any great extent, it will be seen that the peripheral cells of the external portion of the Choreocolax frond present an appearance different from those in the interior. They have become arranged in a regular layer one cell deep over the entire surface of the frond, covering the more or less promiscuous mass of cells beneath (Fig. 4). The internal cells divide and grow to some extent, but it is from the outer, regular layer of cells that the larger part of the exterior portion of the frond is to be developed. The growth inside of the host plant also helps in the formation of this part of the frond, but it is only for a short time that it can be distinguished from the growth of the peripheral cells just mentioned. As soon as the cells which arise from the inner filaments make their way between the cells of the Polysiphonia to the outside, they become arranged in this regular order and blend with the rest of the frond, becoming indistinguishable from it. Cases have been seen where, owing to irregular growth, they did not unite; and then, instead of one large protuberance, there were many smaller swellings closely bunched together. The surface of the young frond, at first almost a plane, becomes rapidly convex by the more active growth of the cells in the centre of the frond. Finally, the hemispherical or almost spherical mass is formed in which the fruit is later borne.

The ordinary method of growth of the frond in distinction to the manner of development in its earlier stages is now to be considered. It is essentially the same after the condition is reached where the peripheral cells are arranged in a distinct layer. Before that time the growth is irregular and unequal. Taking a single peripheral cell and following its growth throughout, we find the method to be as follows. First, the cell is divided into two parts by the formation of a transverse wall. The lowest half of the cell does not divide again, but merely increases in size. The upper cell, on the other hand, is soon divided in two by the formation of a vertical wall, and these two cells ultimately become four by the division of each into two, in a vertical direction at right angles to the first vertical division (Fig. 6). The four cells thus formed repeat the process of division first described, and by this means the frond is enlarged in all three dimensions. The number of cells into which the outer row of cells may divide vertically is not necessarily four. There may be only three, or sometimes as many as five cells so formed, but the important point is that they are equally distributed, so that, besides extending the frond vertically, they increase it almost equally in both of the other directions of space. Other irregularities are also noticeable; sometimes the transverse division fails to take place in some of the cells, and leaves a conspicuously long and ill-shapen cell, which, however, continues its growth like the others. At the time of the most rapid growth the formation of the walls follows so quickly on one another that the newly formed cells do not reach their full size before they divide again. As a consequence of this the outer portion of an actively growing frond is made up of groups of small, closely compacted cells, each group having originated from the division of a single terminal cell (Fig. 5). The cells of these groups gradually grow and assume the normal appearance, the outer ones continuing to divide, though more slowly than before, and the inner ones losing themselves in the inner mass of the frond. The activity of the terminal cells almost entirely ceases as the frond approaches maturity, and in the adult frond there is no sign of further growth.

The tetrasporic fruit of Choreocolax was, as has been said at the beginning of this paper, first mentioned by Farlow, who gives a brief account of it. The tetrasporic fronds were not uncommon in the material I collected at Nahant, and material was easily found from which to study them. They were no more frequent at one time than at another, during the portion of the year in which I looked for them. Externally, the tetrasporic plants present no characters by which they may be invariably distinguished from sterile specimens. The size of the frond bears very little relation to the presence of even mature tetraspores, for it is not at all unusual to find in a very minute frond not a millimeter in diameter tetraspores which are to all appearance perfectly developed. A vertical section of one of the hemispherical swellings shows the tetraspores to be located on the extreme periphery of the frond (Fig. 8). There is no definite limit to the number of tetraspores to be found in a single specimen; sometimes there are very few of them, while at other times there are so many that they have quite crowded the terminal cells out of place. All stages of growth of the tetraspores are present in one frond at the same time, so that their development is not hard to trace. They arise from the enlargement of certain of the terminal cells, but there is no criterion by which it is possible to tell what ones will develop into tetraspores. The first indication is a slight swelling of those cells which are to form the spores (Fig. 9). They rapidly increase in size, the contents of the transforming cells at the same time taking on a more granular appearance than their unmodified neighbors (Fig. 10). After the single cell has attained almost the size of the mature spore, a transverse wall is formed across it (Fig. 11), and is soon followed by a vertical one, which thus divides the spore into four parts, producing a very typical cruciate tetraspore (Fig. 12). Sometimes in the two-celled stage the longitudinal division of the distal cell precedes that of the proximal one, giving the spore the appearance of being tripartite. The longitudinal wall of the proximal cell is ultimately formed, however, and then the spore presents the usual cruciate aspect. True cases of tripartite spores are to be found, however, where the longitudinal division of the lower cell has actually taken place in a direction at right angles to that of the upper one (Fig. 13). The contents of the tetraspores do not differ very markedly from those of the other cells, except that they are more highly granular. Fully adult spores from fresh specimens are usually of a brownish color, and measure on the average 45.5 × 28 μ. Some apparently mature ones were much smaller, being only 25 × 18 μ. The curious case of distortion of the tetraspores where they were so enormously elongated has already been noted; they measured about 80 μ long by 15–20 μ broad. The tetraspores make their way out by the breaking away of the outer cellulose skin, which becomes very weak as the frond increases in age, and may then be easily ruptured by slight pressure. Attempts were made to germinate the tetraspores, but all proved unsuccessful. It may have been that the conditions were unfavorable, or perhaps that the tetraspores rest some time before germinating

Besides the tetraspores, no one, so far as I am aware, has ever given an account of the reproductive organs of *Choreocolax Polysiphoniæ.* When it was found that the non-sexual reproduction of *C. Polysiphoniæ* was by means of tetraspores, this alga could be classed with much more certainty among the Florideæ, and it was reasonable to suppose that cystocarps might be found on further search. It was, indeed, with this possibility in view that I was led to investigate *C. Polysiphoniæ.* In all of the material collected during the fall and early winter of 1890, nothing but the tetrasporic fruit was noticed. Some specimens obtained at Nahant, on December 11th, proved more interesting. In a few of the fronds, structures were found which at once appeared could be nothing else than cystocarps. These observations were corroborated later, and more cystocarpic material was procured, which enabled me to make out definitely the structure of the fruit, and to some degree also its development. It was not until much later that the trichogynes were first seen, and as it was not possible to trace out the complete course of development from the trichogyne to the ripe cystocarp, it will be best to begin with a description of the latter.

The ripe cystocarpic fronds can usually be distinguished from the others by the fact that they are more or less lobed, each lobe containing a single cystocarp (Fig. 2). This is not a very reliable distinction, however, for when a frond contains only one cystocarp, which not infrequently happens, its shape closely resembles that of a tetrasporic or sterile frond. On the other hand, the other fronds are sometimes lobed, from abnormal conditions of growth, in manner not unlike the cystocarpic specimens. Thus it will be seen that it is impossible to tell certainly, without microscopic examination, in what state any particular frond may be. In the majority of the cystocarpic fronds there are several — from two to five — cystocarps present, though a considerably larger one is, as has already been said, often found in place of many.

Although it might seem to indicate, from the division of the frond into lobes, that the cystocarps are in this instance external, closer search shows that this cannot be considered to be the fact; the growth of so large a body as the cystocarp in so small a frond naturally necessitates the condition found, and even as it is the lobes represent more than merely the conceptacles themselves, for the ordinary tissues of the frond go in part to make them up (Fig. 14). The cystocarps are ovoid to almost spherical in shape, with the smaller end external. They may be readily separated from the surrounding cells by a little careful dissection, when they appear as small white dots, scarcely visible to the naked eye. From a vertical section of a cystocarp a very good idea of its structure may be obtained (Fig. 14). The cells surrounding the cavity in which the spores are borne are seen to be more closely compacted than those of the rest of the frond, and of a different shape. This closely compacted wall consists chiefly of sterile cells, with which on the inner surface the spore-bearing cells are intricately associated. The conceptacular wall is always thickest at the inner end of the cystocarp, gradually becoming thinner as it approaches the outside, being represented in the region of the carpostome by a single layer of cells. The carpostome, which has always been seen in these cystocarps, consists of a small circular opening through the cellulose covering of the frond. It is situated at the small end of the cystocarp, where it approaches nearest the exterior of the frond. The cells which compose the wall of the cystocarp, when viewed in vertical section, are seen to be either spindle-shaped or very thin and almost filiform (Fig. 14). This is due to the collection of the protoplasm of the cell at the centre, leaving but a small amount at the extremities. Other aspects show the cells to be flat or tabular, with often a very irregular outline. They may then, in a general way, be said to be of a lenticular shape, although they do not often approach the circular in form. They always lie with their flattened faces presented to the interior surface of the cystocarp, and consequently a vertical section, if it be not tangential, always exhibits the cells in their fusiform appearance. The amount of gelatinous intercellular substance between these cells is much smaller than is found elsewhere, except perhaps in the growing terminal part of the frond.

It is on cells very like the ones just described, perhaps somewhat thicker in proportion to their other dimensions, that the carpospores are borne. The cells from which the spores arise lie directly inside of the conceptacular wall, and are, as has previously been said, closely interwoven with it. They have no peculiarities in shape or structure which distinguish them from the sterile cells forming the wall. They do not, however, like the latter, always present their flat faces inwards, but are more irregularly arranged. The spores are borne from the ends or angles of the cells, or from protuberances arising from their flat surface (Figs. 15, 16). The entire surface of the cavity is lined with the spores, except in the immediate neighborhood of the carpostome (Fig. 14). They are not arranged in chains, but are borne singly. In shape they are irregularly ovoid or pyriform, with tapering and sometimes acute apices. A small basal cell is always found between the spores and the spore-bearing cells proper. From the basal cell there arises a sterile filament that always appears to be present (Figs. 15, 16). This paraphysis is usually somewhat longer than the spore, but as it arises from the side, and not the top, of the basal cell, it extends out no farther. Its contents are almost hyaline, in contrast with those of the spore. In the mature cystocarp the spores are directed inwards, and somewhat upwards, towards the carpostome, almost completely filling the cavity. The ripe spores are highly granular, somewhat darker in color than the other tissues of the plant, and have distinct nuclei. That the cystocarps examined were ripe, there can be no doubt. Some specimens collected on December 23d were placed uninjured in sea-water on a slide; when they were examined, some fifteen hours afterwards, many spores were found to have made their way out of the cystocarp, and to be lying loose in the surrounding water. Attempts were made to germinate the carpospores as well as the tetraspores, all of which failed, owing, no doubt, to the same causes suggested in the case of the tetraspores.

Before leaving the subject of the cystocarps, it is necessary to describe a peculiar condition of the frond that was always found in cystocarpic plants. In the peripheral portion of such a frond, instead of finding the usual elongated pyriform cells, one sees a large number of small spherical ones arranged in distinct chains (Figs. 14, 17). The transition between the two conditions can be traced without much difficulty, in fronds where the cystocarps have just commenced to develop. It is seen that, when the main part of the growth of the plant has taken place, the terminal cells, instead of dividing as frequently vertically, divide more frequently transversely, forming short chains of small cells, which afterwards increase considerably in size. Frequently even in the adult fronds the chains of terminal cells are seen to give place to the ones of the usual form at the base of the frond (Fig. 14). There is nothing remarkable in the appearance of the walls or the contents of these chains of cells that would lead one to suppose that they have any special function. The condition of the cells seems merely to be that which is very often seen in the cystocarps of other algæ, where the outer wall of the conceptacle consists of a great number of small cells in chains. In the case of *C. Polysiphoniæ*, the frond is so small in proportion to the cystocarp that the whole of it becomes modified in this change.

It was not until late in the course of my examination of *C. Polysiphoniæ* that I discovered the trichogyne and its accompanying organs. The fronds containing them were searched for diligently, but only a few plants were found that were in the right condition. It was undoubtedly too late in the season when I first found the trichogynes to expect them to be common, for then almost all of the cystocarpic fronds were mature. In spite of this, however, sufficient material was found to make out the structure of the undeveloped procarp, and to some extent to follow its development. The trichogyne forms the distal extremity of an irregular chain of cells, which are often connected into a more distinct filament than is common with the interior cells of *C. Polysiphoniæ.* It represents and is developed out of one of a number of cells, which at first were ordinary terminal cells like the others of the frond. The terminal cells arising from the same basal cell as the developing trichogyne and trichophoric apparatus apparently cease all growth after the latter begin to develop, and soon become buried in the frond. One or more of them often remain, as in Figures 18, 19, and 21, *c*. The remaining cell which is to continue the growth divides, the terminal cell developing into the trichogyne, the lower ones forming the trichophoric apparatus. When fully developed, the trichogyne is very long. The cell itself is about 2–2.5 μ in diameter, and often 115 μ long. The diameter of the trichogyne is much greater, however, by reason of a very thick apparently gelatinous sheath of high refrangibility. The whole trichogyne, including sheath, measures 5–6 μ broad. At the apex the sheath becomes much thinner, and consequently does not materially increase the length of the trichogyne. The cell of the trichogyne is often irregular in diameter, frequently exhibiting considerable swellings, which however are not followed by similar swellings in the sheath (Fig. 19). At the base the cell broadens out where it joins the trichophoric apparatus (Figs. 18, 19). The trichogyne usually pierces the cellulose covering without bending or other distortion, and extends for a considerable distance beyond the frond. Not infrequently, however, the trichogynes instead of immediately making their way through the sheath, become bent when they come in contact with its lower surface. They often grow for considerable time between the outer layer of terminal cells and the under surface of the cellulose covering before they succeed in breaking through it. Below the trichogyne are three trichophoric cells. They are usually somewhat wedge-shaped cells, of variable size. The order of their formation I do not know. The one next to the trichogyne is generally smaller than the others, and is set at somewhat of an angle to them (*a*, Figs. 18, 19). In other words, the axis of the procarp curves here. The other two cells of the trichophore lie side by side, and are usually of about the same size (a', a'', Figs. 18, 19). The trichophoric cells are of a decided brownish color, and their contents are quite clear. The cell *b* (Figs. 18, 19), on which the lowest of the trichophoric cells rest, presents very much the appearance of the cells of the rest of the frond. The cells *c* (Fig. 18, 19, 21) I take to be undeveloped terminal cells, previously referred to in the development of the trichogyne. The cell *b*, and apparently in some cases a number of the cells beneath it, are probably the carpogenic cells of the procarp. In all the cases seen it did not seem that the trichophore played any part in the formation of the cystocarp. In Figure 20 the cells a, a', a'', probably correspond to the trichophoric cells indicated by the same letters in the other figures. If this is the case, the fate of the trichophoric cells can be accounted for. After fertilization they shrivel up and finally disappear, without developing further. In the same figure *tr* indicates probable remnants of the trichogyne, while the cells b', b'', and b''' also are the outcome of the division of the original carpogenic cell *b* (Figs. 18, 19). Some cases were observed where the growth of the cystocarp seemed to originate even farther down in the tissue of the plant, but nothing definite was established concerning this. After the stage represented in Figure 20, the development becomes hard to trace. In the next one figured (Fig. 21), the cells *b*, *b'*, *b''*, etc., are probably to be compared with those indicated by the same letters in the previous figure, while *c* is an undeveloped terminal cell before noticed. The cells *b'*, *b''*, etc., have increased enormously in size and in number as well. They have given rise to many smaller cells the fate of which seems probably to be the formation of the cystocarp proper. The course of growth becomes now even more obscure. The cells in the neighborhood of the young cystocarp become complicated in the growth of the wall, and effectually hide the changes which at this time are affecting the cystocarp proper. It seems probable from what was seen that the cells *b*, *b'*, *b''*, etc., start up another growth, and, budding outwards, form, with the surrounding cells whose growth has been already mentioned, the wall of the tabular cells found in the ripe fruit. The small cells first formed from the activity of the cells *b*, *b'*, *b''*, etc., are enclosed in this mass, and develop into the spores and spore-bearing cells. It is to be regretted that the material was so scanty for this work. A search will be made next fall earlier in the season, to find if possible more trichogyne-bearing fronds, and an attempt made to determine more definitely the development of the fruit.

Up to the present time the relationship of *C. Polysiphoniæ* to the rest of the Florideæ has been very uncertain. Heretofore, it will be remembered, nothing but tetraspores has been described. In his list of the Florideæ, Schmitz places it among the Gelidiaceæ with Binderella in the sub-order Binderelleæ. His reason for placing it in the Gelidiaceæ is presumably on account of its general likeness to *Harveyella mirabilis* (Reinsch), Schmitz and Reinke, which in the same list is placed in a separate sub-order, Harveyelleæ, next to the sub-order to which Choreocolax is assigned. Others have followed him in this arrangement, but no one, so far as I know, has placed *C. Polysiphoniæ* in any other order of the Florideæ. In view of what has been described in this paper regarding the structure of the cystocarp, this can scarcely be considered to be its true place. The cystocarp of Harveyella is likened by Schmitz, in his note in Reinke's "Algen Flora der westlichen Ostsee," to that of Caulocanthus, a resemblance which would place Harveyella without doubt among the Gelidiaceæ. It certainly seems impossible to consider the cystocarp of *Choreocolax Polysiphoniæ* as closely related to that found in the Gelidiaceæ. It lacks the most essential feature of similarity to the Gelidiaceæ in the absence of the complicated axial placenta which characterizes that order. The carpospores of *Choreocolax Polysiphoniæ,* it will be remembered, were found to be borne singly all over the inner surface of the cavity, on cells or filaments projecting into its cavity. This fundamental difference in structure certainly makes it impossible to consider *C. Polysiphoniæ* one of the Gelidiaceæ. The condition of the cystocarp approaches far more nearly that found in the Chætangiaceæ than in any other order. I examined cystocarpic specimens of *Chætangium ornatum,* in order to compare them with those of *Choreocolax Polysiphoniæ.* Although the cystocarp of Chætangium is somewhat more complicated than that of Choreocolax, there is a great resemblance between the two. The spores are borne in Chætangium on filaments projecting into the cavity of the cystocarp, much in the same way as was observed in *Choreocolax Polysiphoniæ.* The filaments in Chætangium protrude farther into the cystocarpic cavity than in the other form, but that is not an essential difference. The spores themselves resemble those of *Choreocolax Polysiphoniæ* in shape, but are much smaller. Galaxaura was also examined, and an even closer resemblance seen. The cystocarp of Galaxaura is simple, like that of *Choreocolax Polysiphoniæ,* and the spores are larger than those of Chætangium. The dissimilarity of the fronds found in the various genera of the Chætangiaceæ from that of *Choreocolax Polysiphoniæ* can only be considered as a specific distinction, and not as a valid objection against placing the plant in question in this order. The fronds of the forms already included under the Chætangiaceæ are so dissimilar that there cannot be said to be any typical frond in this order.

Before closing, it seems well to say a few words regarding the methods of work employed in investigating this rather unmanageable alga. The immense amount of gelatinous matter in the frond was of course a most difficult thing to preserve properly. Ordinary methods of killing with corrosive sublimate and chromic and picric acids were tried, and yielded partially satisfactory results. The material thus killed was useful for maceration and dissection. All these reagents, however, caused a great amount of shrinkage in the tissues of the plant. Many other methods that seemed suitable were tried with a hope of finding some reagent that would kill the cells and leave them in a natural condition. Nothing was discovered, however, that served this purpose ; in fact, it was found that just as soon as the cells of the plant died, however cautiously they may have been killed, just so soon did they shrink and contract into the grotesque shapes one finds them in. More than this nothing could be found that would swell up the contracted tissues to their lifelike appearance. Potassic hydrate caused a general disintegration, and the various acids, unless used so strong as to dissolve the whole mass, produced but little effect. For this reason, the greater part of the work was done with sections cut between pith, in sea-water, with a razor. Nothing else than sea-water was allowed to touch them, and by this means sections were obtained that would keep alive three or four hours, after which time they gradually contracted as they died. Almost all the drawings were made from these fresh sections, and whatever work was done with dried or alcoholic material was verified by means of them. Many false appearances are given by the immense contraction which takes place when the frond dies, and it was for this reason that these precautions were taken. In order to have a supply of fresh material constantly on hand, I made excursions as often as possible during the winter to Nahant, where *Choreocolax Polysiphoniæ* is fairly abundant. The Choreocolax and the Polysiphonia on which it grew could with care be kept for a considerable time, either in sea-water or moist in a tin box. The latter way is perhaps the better, and if the box is kept moderately cool, and has been well sterilized before putting the material in it, the Choreocolax will keep alive from ten days to two weeks.

In conclusion, I wish to thank all those who have kindly helped me in my work. To Professor W. G. Farlow I am especially obliged, and to Dr. W. A. Setchell I am also indebted for several valuable suggestions.

Cryptogamic Laboratory, Harvard University,
March, 1891.


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EXPLANATION OF FIGURES.

Fig. 1. Typical form of frond. × by about 3 diam.
" 2. Lobed cystocarpic frond. × by about 3 diam.
" 3. Very young frond just making its way into the Polysiphonia. × 180.
" 4. Somewhat older stage, where cells are more regularly arranged. × 200.
" 5. Terminal cells of growing frond, from maceration preparation. × 350.
" 6. Diagrams showing method of growth of terminal cells.
" 7. From a preparation shrunk in glycerine to show connection of cells of parasite with host. × 150.
" 8. Vertical section of tetrasporic frond. × 150.
" 9, 10, and 11. Three stages in the development of tetraspore. × 350.
" 12. Adult cruciate tetraspore. × 350.
" 13. Adult tripartite tetraspore. × 350.
" 14. Vertical section of cystocarpic frond. × 150.
" 15 and 16. Showing the two ways in which the carpospores are borne. × 350.
" 17. Portion of periphery of cystocarpic frond, showing chains of cells. × 350.
" 18. Young procarp. × 600.
tr, trichogyne.
a, *a*,′ *a*,″ trichophoric cells.
b, carpogenic cell.
c, undeveloped terminal cell.
" 19. Older procarp with fully developed trichogyne. × 600.
References as in Figure 18.
" 20. Procarp in which carpogenic cells have begun to develop. References as in Figure 18, except b', b'', b''', which are the cells newly formed from the carpogenic cell *b*. × 600.
" 21. More advanced stage in development. References as before. b'''', b^{v}, etc., are the result of further proliferation of cells *b*, b', etc. × 600.

Figures 1 and 2 were drawn free hand. The others were all drawn with the camera, except Figure 6, which is merely a diagram. Figures 18 to 21 have been reduced one third from the original drawings. All the drawings are from fresh material except Figures 6 and 7, the latter of which was drawn from a section shrunk in glycerine.

VI.

ON THE MATRICAL EQUATION $\phi\,\Omega = \Omega\,\phi$.

By HENRY TABER, CLARK UNIVERSITY.

Presented by Prof. W. E. STORY, May 26, 1891.

FOR a given matrix, Ω, the most general matrix ϕ satisfying the equation $\phi\,\Omega = \Omega\,\phi$ may be found by the consideration of the canonical form of the matrix Ω. If the distinct latent roots of Ω are g_1, an m-tuple latent root, g_2, an n-tuple latent root, etc., the canonical form of Ω is $\omega\,\theta\,\omega^{-1}$, where

$$\theta = \begin{pmatrix} \boxed{\theta_1} & & \\ & \boxed{\theta_2} & \\ & & \ddots \end{pmatrix}$$

in which all the constituents are zero except those in the square arrays θ_1, θ_2, etc., which correspond, respectively, to the latent roots g_1, g_2, etc., and are severally of order equal to the multiplicity of the latent root to which they correspond; and if the characteristics of the latent root g_1 are $(m\,;\ p, q, r, \ldots\ s, t)$, then

$$\theta_1 = \begin{array}{c|c|c|c|c|c|c|}
 & p & q & r & & s & t \\ \hline
p & \begin{matrix} g_1 & 0 & \dots & 0 \\ 0 & g_1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 0 \end{matrix} & \begin{matrix} 1 & 0 & \dots & 0 \\ 0 & 1 & . & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 0 \end{matrix} & & & & \\ \hline
q & & \begin{matrix} g_1 & 0 & \dots & 0 \\ 0 & g_1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & g_1 \end{matrix} & \begin{matrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 0 \end{matrix} & & & \\ \hline
r & & & \begin{matrix} g_1 & 0 & \dots & 0 \\ 0 & g_1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & g_1 \end{matrix} & & & \\ \hline
 & & & & \ddots & & \\ \hline
s & & & & & \begin{matrix} g_1 & 0 & \dots & 0 \\ 0 & g_1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & g_1 \end{matrix} & \begin{matrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 0 \end{matrix} \\ \hline
t & & & & & & \begin{matrix} g_1 & 0 & \dots & 0 \\ 0 & g_1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & g_1 \end{matrix} \\ \hline
\end{array}$$

where the letters on the left and above denote the number of rows and columns in the respective squares and rectangles below and to the right. Similarly with respect to the square arrays θ_2, etc., corresponding to the other latent roots.* If, now, ϕ is a matrix commutative with Ω, the most general expression for ϕ is $\phi = \omega \, \eta \, \omega^{-1}$, where

$$\eta = \left(\begin{array}{cccc} \boxed{\eta_1} & & & \\ & \boxed{\eta_2} & & \\ & & \ddots & \\ & & & \end{array} \right)$$

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* This representation of a matrix, what I term its canonical or standard form, was, I believe, first given explicitly by Weyr, Comptes Rendus, Vol. C.; it was, however, given substantially by Buchheim, earlier, in Proc. Lond. Math. Soc., Vol. XVI.

in which all the constituents are zero except those in the squares along the principal diagonal, and

$$\eta_1 = \left|\begin{array}{ccc|ccc|ccc|c}
a_{11}\; a_{12} & \cdots & a_{1p} & b_{11}\; b_{12} & \cdots & b_{1q} & c_{11}\; c_{12} & \cdots & c_{1r} & \\
a_{21}\; a_{22} & \cdots & a_{2p} & b_{21}\; b_{22} & \cdots & b_{2q} & c_{21}\; c_{22} & \cdots & c_{2r} & \text{etc.} \\
\cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \\
a_{p1}\; a_{p2} & \cdots & a_{pp} & b_{p1}\; b_{p2} & \cdots & b_{pq} & c_{p1}\; c_{p2} & \cdots & c_{pr} & \\
\hline
 & & & a_{11}\; a_{12} & \cdots & a_{1q} & b_{11}\; b_{12} & \cdots & b_{1r} & \\
 & & & a_{21}\; a_{22} & \cdots & a_{2q} & b_{21}\; b_{22} & \cdots & b_{2r} & \text{etc.} \\
 & & & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \\
 & & & a_{q1}\; a_{q2} & \cdots & a_{qq} & b_{q1}\; b_{q2} & \cdots & b_{qr} & \\
\hline
 & & & & & & a_{11}\; a_{12} & \cdots & a_{1r} & \\
 & & & & & & a_{21}\; a_{22} & \cdots & a_{2r} & \text{etc.} \\
 & & & & & & \cdot\;\cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot\;\cdot & \\
 & & & & & & a_{r1}\; a_{r2} & \cdots & a_{rr} & \\
\hline
 & & & & & & & & & \text{etc.}
\end{array}\right|$$

the a's, b's, c's, etc. being arbitrary; the mode of filling up the remaining squares along the principal diagonal and the rectangles above the principal diagonal is obvious. A similar expression obtains for η_2, etc.

WORCESTER, May 26, 1891.

VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE PRODUCTS OBTAINED BY THE ACTION OF NITRIC ACID UPON BROMTRINITROPHENYLMALONIC ESTER.

By C. Loring Jackson and W. B. Bentley.

Presented May 13, 1891.

Our attention was first called to this subject by the appearance of a vivid red color, when common strong nitric acid was used to set free bromtrinitrophenylmalonic ester from its sodium salt, whereas no such color was observed if hydrochloric or sulphuric acid was used in place of nitric. Upon studying this action, we soon found that a new compound was formed, which could also be obtained from the free bromtrinitrophenylmalonic ester by treating it with hot nitric acid for a few minutes,* or for some hours in the cold; the free ester therefore acts with nitric acid less readily than its salt, for with that the color appeared immediately. The further study of this compound (which was obtained in colorless prisms) proved that its formula was $C_6HBr(NO_2)_3CNO_2(COOC_2H_5)_2$; that is, that it had been formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the group NO_2. We have also obtained the following similar derivatives: from the bromdinitrophenylmalonic ester $C_6H_2Br(NO_2)_2CNO_2(COOC_2H_5)_2$, melting point 111°, and from the trinitrophenylenedimalonic ester $C_6H(NO_2)_3CNO_2(COOC_2H_5)_2CH(COOC_2H_5)_2$, also melting at 111°, so that the reaction seems to be a general one. The position of the group NO_2 introduced by the action of nitric acid was determined by the study of the acidity of these compounds. In the bromtrinitrophenylmalonic ester $C_6HBr(NO_2)_3CH(COOC_2H_5)_2$ there are only two atoms of hydrogen, one on the benzol ring, the other on the side-chain; if the first of these were replaced by NO_2, the effect, if any

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* A preliminary account of this substance forms part of a paper by G. D. Moore, and one of us (these Proceedings, XXIV. 265). The statements made there are superseded by this paper.

would be to increase the acidity of the compound; whereas if the atom of hydrogen on the side-chain were replaced, the substance would cease to show acid properties, as the NO_2 would have taken the place of the only atom of hydrogen which can be replaced by a metal. Upon studying the behavior of the new compound with alkaline reagents, we found that none of them affected it in aqueous solution, and that it was acted on only by sodic hydrate or ethylate in alcoholic solution, thus showing a marked contrast to the behavior of bromtrinitrophenylmalonic ester, which is acid enough to decompose sodic carbonate in aqueous solution. As just stated, sodic hydrate or ethylate does act upon our substance, but the red solution formed by the sodic ethylate was proved to contain sodic nitrite, and therefore the formation of the red salt was preceded by the removal of the group NO_2, which proves that this radical has replaced the hydrogen of the side-chain, as represented in the formula given above. This result was confirmed by the study of the compound $C_6H_2Br(NO_2)_2CNO_2(COOC_2H_5)_2$, which proved even less susceptible to the action of alkalies than the corresponding trinitro compound. The replacement of the hydrogen in the malonic ester radical is not at all strange, since Franchimont and Klobbie * have found that nitric acid converts malonic ester into nitromalonic ester.

To determine whether our substances were nitro compounds, that is, with the radical NO_2 attached to the side-chain by its nitrogen, or nitrites, that is, with the radical attached by one of its atoms of oxygen, we considered in the first place the further action of nitric acid upon the compound $C_6HBr(NO_2)_3CNO_2(COOC_2H_5)_2$, which converted it after warming for three hours into $C_6HBr(NO_2)_3COH(COOC_2H_5)_2$, that is, the bromtrinitrotartronic ester; the reaction seemed to run smoothly, and the yield was 40 per cent of the theory. A similar change was produced by heat; when exposed to a temperature of 124°–126°, the substance melted, turned blood-red, and gave off a great deal of gas, with a striking increase in volume at the same time.† A study of the gases showed that a part of the substance

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* Ber. d. ch. G., XXIII., R. 62 from Rec. Trav. Chim., VIII. 283. For a discussion of the effect of different radicals upon the action of nitric acid on fat substances, see Franchimont, Ber. d. ch. G., XX., R. 689 from Rec. Trav. Chim., VI. 224, and Ber. d. ch. G., XXIII., R. 64 from Rec. Trav. Chim., VIII. 307.

† These phenomena shown by our substance in melting, as well as many of its other properties, are very similar to those observed by Gabriel in the cases of the benzylidenphthaliddinitrite, Ber. d. ch. G., XVIII. 1255, and the ethindiphthaliddinitrite, Ber. d. ch. G., XIX. 837, which confirms the view that our substance is a nitrite.

had undergone complete decomposition, as they contained bromine; the residue, however, furnished a considerable amount of the substituted tartronic ester mentioned above. The action therefore has a certain resemblance to the conversion of the nitrate of tartaric acid into tartronic acid. These easy conversions of the compound containing the group NO_2 into the corresponding tartronic ester can be best explained on the theory that this group is attached to the side-chain by oxygen, but cannot be considered as a strict proof of this point. Accordingly we have reduced with tin and hydrochloric acid the substance $C_6H_2Br(NO_2)_2CNO_2(COOC_2H_5)_2$ (selected because it can be obtained more easily than the trinitro compound), and have found that it yields ammonic chloride and a substance having the formula $C_6H_3NH_2(CHOHCONH)HCl$, that is, the chloride of amidoxy-oxindol; there can be no doubt, therefore, that the group NO_2 is attached to the side-chain by one of its atoms of oxygen, and the substances are nitrites and not nitromalonic esters.

One of the most striking properties of the nitrite of bromtrinitrophenylmalonic ester is its slight stability. As has been already stated, it decomposes rapidly, with change of color and evolution of gas, at 124°–126°, but it is not necessary to heat to this temperature to bring about the decomposition, as it also takes place slowly at 100°, and partially even at 70°. Boiling with alcohol decomposes the substance completely, and boiling water produces a similar but less complete change. The nitrites of the corresponding dinitro compound and of the trinitrophenylenedimalonic ester are much more stable.

As has been stated above, the nitrite of bromtrinitrophenylmalonic ester, if warmed for three hours with strong nitric acid, or heated alone to its decomposition point, yields a product in which the radical of the nitrous acid has been replaced by hydroxyl, and which is therefore bromtrinitrophenyltartronic ester; this substance melts at 156°, and possesses marked acid properties. It is not necessary, however, to make it from the nitrite, as the bromtrinitrophenylmalonic ester is converted directly into it by warming for three hours with nitric acid. This therefore is a case of the direct oxidation of a tertiary hydrogen to hydroxyl,* and, as we have succeeded in isolating the intermediate product, our work throws some light on the mechanism of the reaction, showing that it consists in the case of nitric acid of the formation of a nitrite, followed by its saponification to the hydroxyl compound.

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* Richard Meyer, Ann. Chem., CCXIX. 234, CCXX 1; J. Bredt, Ber. d. ch. G., XIV. 1780.

$C_6H(C_6H_5NH)(NO_2)_3CNO_2(COOC_2H_5)_2$, the nitrite of anilidotrinitrophenylmalonic ester, was obtained by the action of aniline on the corresponding bromine compound; it forms red rhombohedra, which melt at 119°, decomposing at one degree higher, and shows marked acid properties, which must be due to the effect of the three nitro groups upon the hydrogen attached to the nitrogen in the anilido group, since, as has been already stated, the corresponding bromine compound forms no salts. This conclusion was confirmed by the study of the anilidotrinitrotoluol, which contains no other hydrogen capable of being replaced by a basic radical, and yet formed the sodium salt $C_6CH_3H(C_6H_5NNa)(NO_2)_3$. As was to be expected, however, this toluol compound was not so acid as the nitrite of anilidotrinitrophenylmalonic ester, which contains such a very negative radical in place of the methyl.

The anilidotrinitrotartronic ester was also made from the corresponding bromine compound, and was obtained in two modifications; one formed at higher temperatures appeared in orange-red prisms melting at 143°, the other in rounded masses of yellow needles melting at about 122°. Both show the same percentage composition on analysis, and one is easily converted into the other; the yellow into the red by allowing the alcoholic solution to crystallize at about 60°, by heating the solid a little below its melting point, or by boiling it with water; the red into the yellow by solution in glacial acetic acid and precipitation with water. Unfortunately we have not succeeded in determining the molecular weights of these substances, as we have not yet found a solvent that gives satisfactory results with Raoult's method. The work on these substances will be continued in this laboratory, especially with a view to determining whether the nitrogen is the cause of the isomerism (if they are not polymeres), but we may say now that this does not seem very probable to us on account of the striking resemblance in properties * between our two substances and the two forms of benzilorthocarbonic acid described by Graebe.†

The anilidotrinitrophenyltartronic ester forms salts with one atom, $C_6H(C_6H_5NH)(NO_2)_3COM(COOC_2H_5)_2$, or with two atoms of univalent basic radicals, $C_6H(C_6H_5NM)(NO_2)_3COM(COOC_2H_5)_2$. To our great surprise, the disodic salt was formed even when the ester was present in large excess. This tartronic ester is much more strongly acid than the anilidotrinitrophenylmalonic ester (melting

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* It is a curious fact that even the melting points are nearly the same.

† Ber. d. ch. G., XXIII. 1344.

point 133°), a fact which confirms the formula assigned to it. We may add, that we have failed in all our attempts to convert anilidotrinitrophenylmalonic ester into its nitrite, or the corresponding tartronic ester, by the action of nitric acid.

We have also tried without success to convert the bromdinitrophenylmalonic ester into dinitrophenylenedimalonic ester by the further action of sodium malonic ester.

The remainder of the paper contains the experimental details of the work.

Preparation of Tribromtrinitrobenzol.

The experience gained in making tribromtrinitrobenzol for the work described in this paper has led us to introduce into the process given in previous papers * from this Laboratory some improvements, which are described in this section.

To the preparation of tribromaniline we have nothing to add, but in the conversion of it into tribrombenzol we have found it best to proceed as follows: — 50 gr. of dry tribromaniline were dissolved with the aid of heat in 300 c. c. of alcohol containing 75 c. c. of benzol to increase its solvent power, and 20 c. c. of common strong sulphuric acid added to the hot solution from a pipette. If this formed a precipitate, it was dissolved by longer heating, more of the solvents being added if necessary. 20 gr. of finely powdered sodic nitrite were then sifted into the hot liquid, as rapidly as the violence of the action would permit; after which the whole was heated until the effervescence had ceased, and, after standing over night, filtered, washed, and dried, when the product could be treated directly with nitric acid to make the tribromdinitrobenzol in the manner already described.† The yield of tribrombenzol was good, 42–44 gr. from the 50 gr. of tribromaniline. The filtrate and washings contained so little of the organic substance that it was not worth while to work them up.

In the conversion of this body into tribromtrinitrobenzol we have found the cause of the much larger yield obtained by Dr. Moore ‡ than by Dr. Wing.§ This does not depend so much on the larger proportion of fuming sulphuric acid used, as on the rapidity with which the boiling is carried on. To get the best yield we found it necessary to raise the mixture to the boiling point as quickly as possible, and to keep it boiling violently during the whole of the three hours. Under these conditions the yields varied from 8 to 10 gr. of tribromtrinitrobenzol from 20 gr.

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* These Proceedings, XXIII. 139, XXIV. 258, 273.

† Ibid., XXIV. 274.

‡ Ibid., XXIV. 258.

§ Ibid., XXIII. 140.

of tribromdinitrobenzol, that is, 36 to 45 per cent of the theoretical, if both the nitric and fuming sulphuric acids were of the best quality. To prove that this violent boiling was the cause of the large yields, in one experiment the mixture was allowed to stand in the cold for a week, and then kept barely at the boiling point for seven hours, when it yielded only 18 per cent of the tribromtrinitrobenzol.

The Nitrite of Bromtrinitrophenylmalonic Ester, $C_6HBr(NO_2)_3CNO_2(COOC_2H_5)_2$.

This substance was prepared as follows: — 3 gr. of bromtrinitrophenylmalonic ester* were mixed with about 10 gr. of nitric acid, specific gravity 1.38, and warmed in a dish for three minutes on the water bath, when both the undissolved organic substance and the acid became intense blood-red; the mixture was then allowed to cool, the acid liquid poured off, and the solid residue warmed once more for two minutes with about the same volume of fresh acid. After this, the acid was decanted off, and the solid crystalline product washed with water till free from nitric acid, which changed it from a deep blood-red to a pale reddish-white color. The purification of this substance gave us much trouble at first on account of its slight stability, since even the short warming necessary to dissolve it in alcohol was sufficient to decompose it partially, while longer heating with alcohol produced complete decomposition; but at last we obtained satisfactory results from the following method. The crude substance, after the thorough washing with water mentioned above, was dissolved in warm chloroform, in which it is freely soluble, but even with this solvent care must be taken to warm the mixture for as short a time as possible; it was advisable, therefore, to achieve the solution rather by the use of a larger quantity of chloroform than by using a smaller volume at a higher temperature. This chloroform solution was then diluted with about its own volume of common alcohol, when the substance gradually separated in well formed white prisms, and was obtained pure after two of these crystallizations. It must be dried *in vacuo*, as it decomposes on the water bath; in fact, even the temperature of a steam radiator (about 70°) was sufficient to bring about a partial decomposition.

A small additional amount of this substance could be obtained from the red nitric acid mother liquors formed in its preparation, either by adding water or by evaporating them to dryness; but this quantity is

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* Melting at 104°. These Proceedings, XXIV. 258.

so small that it is not worth the amount of work necessary to free it from the red viscous impurity with which it is mixed, especially as the mother liquors can be used to more advantage for the preparation of the bromtrinitrophenyltartronic ester made by the longer action of hot nitric acid on bromtrinitrophenylmalonic ester.*

The same substance was formed when the bromtrinitrophenylmalonic ester stood in the cold with nitric acid of specific gravity 1.38 for three days. At first there was no visible change, but after two hours the mixture began to show a red color, which increased in intensity to a deep blood-red. The product was purified in the way just described, but this method of making it is on the whole not so good as that at a temperature of 100°.

The ease with which the substance breaks up under the influence of heat rendered the combustion of it a matter of great difficulty, since we encountered at one time an almost explosive evolution of gas, and at another the formation of a partial vacuum in the tube. The latter we are inclined to ascribe to the sudden absorption by the plumbic chromate of the large quantity of bromine given off by the substance. We finally succeeded in getting good results by spreading out the weighed portion through the whole length of a long porcelain boat, and then applying the heat so gradually that a layer of not more than a few millimeters of it melted at any one time. Care was also taken that the temperature did not rise much above 115° until the whole of the substance had been melted, after which the combustion was finished in the usual way without trouble.

The analyses led to the following results: —

I. 0.2157 gr. of the substance gave on combustion 0.2514 gr. of carbonic dioxide and 0.0496 gr. of water.

II. 0.1978 gr. of the substance gave 0.2310 gr. of carbonic dioxide and 0.0428 gr. of water.

III. 0.1978 gr. of the substance gave 0.2324 gr. of carbonic dioxide and 0.0430 gr. of water.

IV. 0.2014 gr. of the substance gave 20.6 c. c. of nitrogen at a temperature of 24° and a pressure of 772.6 mm.

V. 0.1890 gr. of the substance gave 18.6 c. c. of nitrogen at a temperature of 19° and a pressure of 752.8 mm.

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* On one occasion the acid mother liquors yielded by spontaneous evaporation large white prisms, which melted in the crude state at about 99°, and were apparently somewhat soluble in water; but, although we have tried in many ways, we have not succeeded in obtaining this substance a second time.

VI. 0.2101 gr. of the substance gave by the method of Carius 0.0813 gr. of argentic bromide.

VII. 0.2078 gr. of the substance gave 0.0792 gr. of argentic bromide.

VIII. 0.2054 gr. of the substance gave 0.0776 gr. of argentic bromide.

	Found.							
	I.	II.	III.	IV.	V.	VI.	VII	VIII.
Carbon	31.79	31.84	32.03					
Hydrogen	2.56	2.40	2.42					
Nitrogen				11.66	11.20			
Bromine						16.47	16.22	16.08

These analytical results agree best with the percentages required by a substance formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the radical NO_2, as is seen from the following table.

	Calculated for $C_6HBr(NO_2)_3CNO_2(CO_2C_2H_5)_2$.	Found. Mean.
Carbon	31.52	31.88
Hydrogen	2.22	2.46
Nitrogen	11.32	11.43
Bromine	16.16	16.26

Our reasons for the position assigned to the radical NO_2 in this formula, and for supposing that it is not a nitro group $(- N \equiv O_2)$, but a nitrite $(- O - N = O)$, have been already stated in the introduction to this paper. The yield is satisfactory on the whole; 5 gr. of bromtrinitrophenymalonic ester gave 3.26 gr. of the substance,* instead of the 5.5 gr. required by the calculation, that is, 59 per cent of the theoretical yield.

Properties of the Nitrite of Bromtrinitrophenylmalonic Ester. — It occurs usually in short thick well developed glistening white prisms, with terminations consisting of two planes at both ends, which seem to indicate that the crystals belong to the monoclinic system. Less commonly the prisms are long and rather slender, with terminations similar to those of the shorter form. Its behavior when heated is very characteristic. If a tube containing some of it is dipped into an oil bath at 124°–126°, the substance turns red round the sides, then deeper, and the action gradually runs through the mass, until after a second or two the whole is melted forming a dark blood-red liquid, which occupies many times the volume of the original substance, and contains bubbles

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* In addition to this amount 0.7 gr. of bromtrinitrophenyltartronic ester was obtained from the mother liquors.

of gas. The action is evidently a decomposition, and can be produced at much lower temperatures, since if the tube containing the substance, instead of being dipped into the heated bath as described above, is gradually heated with the bath, the action takes place even below 120°. In fact, it can also be brought about by long-continued heating in the steam bath, or partially even at 70°. It is evident, therefore, that the compound has no definite melting or decomposition point, but yet the temperature given at first (124°–126°) can be used as such in purifying the substance, since it is essentially constant, if care is taken always to heat the samples examined in the same way.

This decomposition seemed so interesting that we examined it more carefully. For this purpose a considerable quantity of the nitrite of bromtrinitrophenylmalonic ester was heated in a test tube inserted in an air bath, and the gaseous products of the reaction drawn through a solution of baric hydrate. At 103°–108° there was a quantity of red vapor given off, and a precipitate of baric carbonate formed in the tubes containing the baric hydrate solution. The red vapor was recognized by the smell as bromine, and this was confirmed by the precipitation of argentic bromide when argentic nitrate was added to the acidified filtrate from the baric carbonate. On the other hand, we could not detect a trace of nitrate or nitrite with ferrous sulphate and sulphuric acid. After the substance had been heated to 103°–108° for three hours, the temperature was raised to 125° for two hours and a half, but the additional loss at this higher temperature was very small. We intended originally to determine quantitatively the amounts of the various products, but abandoned this idea when we found that the loss was not constant, three experiments giving 25 per cent, 30 per cent, and 21 per cent respectively. The appearance of the bromine, too, shows that there has been a complete decomposition of a part of the substance, and therefore the volatile products are of so little interest that we did not care to spend the time necessary for the identification of the others, which must have been formed in addition to the bromine and carbonic dioxide. On the other hand, we were much interested in the non-volatile product of the reaction left in the test tube as a fused rather viscous mass of a brownish red color, in which crystals were embedded. It was purified by washing several times with alcohol, which removed much of the viscous portion, then the residue was crystallized, first from dilute, and finally from common alcohol, and when pure showed the melting point 156° and the crystalline form of the bromtrinitrophenyltartronic ester described later in this paper. The action of heat on our nitrite, therefore, is similar to the well known conversion of the so-called nitrotartaric acid into tartronic acid.

The nitrite of bromtrinitrophenylmalonic ester is almost insoluble in cold water, perhaps a little more soluble in boiling water; but if the substance was boiled for some time with water, the crystals were converted superficially into a dark red oily substance, and the water gave a slight test for bromine; this decomposition seemed to be due, however, only to the heat (see above), not to the presence of the water. It is slightly soluble in cold, more freely in hot ethyl alcohol, but this solution is easily decomposed by heat, since boiling for fifteen minutes converts the substance completely into a brownish red viscous product resembling half-dried varnish, from which nothing definite could be isolated, and even a very short heating with alcohol is sufficient to form some of this viscous body. Its solubility in methyl alcohol resembles that in ethyl alcohol; it is freely soluble in chloroform, or acetone; soluble in benzol, or glacial acetic acid; slightly soluble in carbonic disulphide; very slightly in ether, and essentially insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol described above. Strong sulphuric acid seems to have no action on it in the cold, or if heated, until the substance decomposes, when it dissolves forming a reddish solution; strong hydrochloric acid has no action on it, either hot or cold, as long as the substance does not decompose; strong nitric acid has little or no action on it in the cold, even when allowed to stand with it for some weeks, when heated to 100° it converts it gradually into the bromtrinitrophenyltartronic ester, as is described in detail later in this paper under the preparation of that substance.

Ammonic hydrate acts on it little, if at all, even when the action is assisted by the addition of alcohol; sodic hydrate in aqueous solution has no action, but if alcohol is added the crystals begin to dissolve slowly, imparting a red color to the liquid but only a partial solution is effected in the cold. From this observation we inferred that no salt was formed until the nitrite was decomposed, and to test the accuracy of this inference we treated some of the nitrite with an alcoholic solution of sodic ethylate, which gave at once a dark blood-red coloration; but even here only a part, and that not the larger part, of the crystals of the nitrite was dissolved; the red solution poured off from the unaltered crystals gave a good test for a nitrite with starch paste, potassic iodide, and dilute sulphuric acid, with ferrous sulphate and sulphuric acid, and by Liebermann's reaction, so that there can be no doubt that sodic nitrite was formed in the experiment.

This proves the correctness of our inference that the substance melting at 124°–126° cannot form salts; and the blood-red salt observed must have been derived from the decomposition product left after the removal of the group NO_2 from our substance. It may be added, that acid or neutral sodic carbonate has no action on the nitrite in aqueous solution, and very little, if any, in presence of alcohol.

Nitrite of Anilidotrinitrophenylmalonic Ester,
$C_6H(C_6H_5NH)(NO_2)_3CNO_2(COOC_2H_5)_2$.

Aniline acts with great violence on the nitrite of bromtrinitrophenylmalonic ester. If the substances are mixed at ordinary temperatures, the action is almost explosive, a good part of the mixture is thrown out of the beaker, and the product seems to be principally carbon. If the mixture is kept cool by immersing the beaker in water, the action goes more mildly, but the product is still very black and impure. We therefore carried on the reaction in ethereal solution with the best results as follows: — 1 gr. of the nitrite of bromtrinitrophenylmalonic ester was mixed with a small quantity of ether, and, disregarding the fact that a portion of the crystals had not dissolved, a slight excess of aniline was added; the ether at once turned red, and the undissolved crystals of the nitrite were taken up, while aniline bromide was deposited in their place. At the end of a few minutes the reaction was complete, and, after washing out the aniline and aniline bromide with water containing a little hydrochloric acid, the ether was allowed to evaporate, when it left a vivid red mass, which was purified by dissolving it in hot chloroform avoiding long heating, and then adding alcohol until the crystals began to separate, as it had been found that this substance, like the corresponding bromine compound, was decomposed by heating with alcohol. After the substance showed the constant melting point 119° it was dried *in vacuo* for analysis.

The combustion of this substance was even more difficult than that of the bromine compound, as it decomposed with almost explosive violence at a temperature a few degrees above its melting point, and did not begin to decompose at all at lower temperatures. We were unable therefore to burn it in an open tube, but at last got satisfactory results by using a closed tube, mixing it with a long layer of plumbic chromate and applying the heat very gradually. Its analyses led to the following results: —

I. 0.1542 gr. of the substance gave on combustion 0.2538 gr. of carbonic dioxide and 0.0678 gr. of water.

II. 0.1494 gr. of the substance gave 18.9 c. c. of nitrogen at a temperature of 24°.3 and a pressure of 752.3 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3CNO_2(CO_2C_2H_5)_2$.	Found. I	II.
Carbon	44.97	44.88	
Hydrogen	3.35	4.88	
Nitrogen	13.80		14.02

In spite of the unsatisfactory number for the hydrogen, these results prove that the substance has the formula which we have assigned to it. The yield was good, 0.9 gr. of the nitrite of the bromtrinitrophenylmalonic ester giving 0.7 gr. of the anilido compound, instead of the 0.92 gr. required by the theory, that is, 76 per cent.

Properties. — The nitrite of the anilidotrinitrophenylmalonic ester is a very beautiful substance, crystallizing in rhombohedra often two millimeters long and one millimeter thick, with a very acute angle, which is frequently, but not always, truncated by a basal plane. The color of the crystals by reflected light is a rich full red, somewhat darker than that of chromic anhydride, by transmitted light orange-red. It melts at 119°, turning black and giving off a few bubbles of gas, if the temperature has not risen above this point; but at 120° it decomposes with such violence that frequently a good part of the substance is thrown out of the capillary melting tube. It is essentially insoluble in cold water, and its solubility does not seem to be increased by heat; very slightly soluble in cold ethyl alcohol, more soluble in hot, but still not freely, the hot solution seems to undergo partial decomposition; more soluble in methyl alcohol, whether cold or hot, than in ethyl alcohol, but not freely even in this; very freely soluble in chloroform; freely in benzol, or acetone; soluble in glacial acetic acid; slightly in ether, or carbonic disulphide; insoluble in ligroine. The best solvent for it is a mixture of chloroform and alcohol. Strong sulphuric acid seems not to act on it in the cold, but when heated with it the substance decomposes, and then dissolves with a blackish color; strong nitric acid does not act on it in the cold, but when hot dissolves it with a yellow color; strong hydrochloric acid has no action on it, whether cold or hot.

The nitrite of anilidotrinitrophenylmalonic ester showed marked acid properties. Acid sodic carbonate in aqueous solution had no action with it, but, if assisted with alcohol, gave a red solution; potassic carbonate behaved in the same way; sodic hydrate turned the crystals black, forming at the same time a brownish solution, which on addition of alcohol became deeper and blackish red, turning in time to blackish brown; ammonic hydrate in aqueous solution gave a red color, but the action was not complete until alcohol was added, when a very dark red solution was formed. The nitrite of anilidotrinitrophenylmalonic ester therefore shows much more acid properties than the corresponding bromine compound, which is indifferent to all these reagents except sodic hydrate in presence of alcohol, and this fact puzzled us at first, until we decided that the hydrogen attached to the nitrogen in the anilido radical (C_6H_5NH) might be rendered acid by the presence of the three nitro groups. That this is the correct explanation of the phenomenon we have proved by preparing and analyzing the sodium salt of anilidotrinitrotoluol, which contains no atom of hydrogen that could be replaced by sodium except the one attached to the nitrogen of the aniline radical. The description of this work will be found in the following section.

An attempt to analyze the sodium salt of the nitrite of anilidotrinitrophenylmalonic ester gave no satisfactory result, owing undoubtedly to the partial formation of sodic nitrite from the organic nitrite by the action of the sodic hydrate used in making the salt.

Sodium Salt of Anilidotrinitrotoluol, $C_6CH_3H(C_6H_5NNa)(NO_2)_3$.

To prepare this salt, 1 gr. of anilidotrinitrotoluol * (melting point 151°) was dissolved in alcohol, and mixed with an alcoholic solution of 0.09 gr. of sodic hydrate, that is, over 0.03 gr. less than the amount required to convert the gram of substance into its salt; a little ether was then added, and the solution of the salt evaporated rapidly to dryness in a narrow beaker sunk throughout its whole length in the steam bath. During the evaporation there was an odor of phenylisocyanide. The dry mass was washed thoroughly with benzol to remove the excess of anilidotrinitrotoluol, the residue dried at 100°, and analyzed. As the salt explodes when heated with strong sulphuric acid, it should be dissolved in water, treated with dilute sulphuric acid, filtered, and the filtrate evaporated to dryness and converted into neutral sodic sulphate.

0.7876 gr. of the salt gave 0.1662 gr. of sodic sulphate.

	Calculated for $C_6CH_3H(C_6H_5NNa)(NO_2)_3$.	Found.
Sodium	6.76	6.84

The salt prepared as described above forms a maroon-black powder, which explodes gently when heated alone, or with strong sulphuric

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* These Proceedings, XXIV. 255.

acid, forming in the latter case a very loose spongy blackish mass. It is soluble in alcohol with a yellowish brown color like that of ferric chloride; insoluble in ether, or benzol; water decomposes the salt almost completely, forming a yellow precipitate and a pale brown solution, which is strongly alkaline. The action of the anilidotrinitrotoluol with alkaline reagents was also studied, and, as was to be expected, no action was obtained with acid, or neutral carbonate of sodium, or ammonic hydrate in aqueous solutions; but if the action was assisted by the presence of alcohol, each of these reagents gave a barely perceptible reddish coloration, so slight in the case of ammonic hydrate that we were doubtful whether there had been any action; sodic hydrate in aqueous solution gave a slight yellow coloration, which, on the addition of alcohol, was at once converted into a very dark blood-red. The acid character of the anilidotrinitrotoluol therefore is much less marked than that of the nitrite of anilidotrinitrophenylmalonic ester, and as the position of the anilido group with regard to the nitro groups is the same in both compounds, we must ascribe this to the presence of the nitrite of the malonic ester radical $CNO_2(COOC_2H_5)_2$, with its large amount of oxygen in place of the indifferent methyl contained in the toluol.

Bromtrinitrophenyltartronic Ester, $C_6HBr(NO_2)_3COH(COOC_2H_5)_2$.

If the nitrite of bromtrinitrophenylmalonic ester, or the ester itself, was heated for some time with nitric acid, it was converted into the corresponding tartronic ester, which we found it convenient to prepare as follows: — 1 gr. of bromtrinitrophenylmalonic ester was mixed with about 10 c. c. of nitric acid of specific gravity 1.38, and heated on the water bath for three hours in a dish covered with a watch-glass, fresh nitric acid being added when necessary to replace that lost by evaporation. At the end of this time the substance was found to be completely dissolved in the small quantity of hot nitric acid left, but upon cooling colorless crystals separated, which, after washing with water, were essentially the pure substance, one recrystallization from alcohol being all that was needed to make them melt at 156°, the constant melting point of this compound. If, as was usually the case, the bromtrinitrophenylmalonic ester was contaminated with acetylenetetracarbonic ester, a yellowish oil was also formed, which however remained dissolved in the nitric acid mother liquor. The amount of the substituted tartronic ester in this mother liquor was so small that it did not pay for the working up.

The bromtrinitrophenyltartronic ester can also be made from the nitrite of the corresponding malonic ester, but this method has no advantage over the preparation direct from the malonic ester described above, except in the case of the nitric acid mother liquors from making the nitrite, which yield on longer heating with nitric acid a small amount of the tartronic ester, and this is worth saving on account of the tedious and costly preparation of the mother substance.

The substance dried *in vacuo* was analyzed with the following results: —

I. 0.1951 gr. of the substance gave on combustion 0.2380 gr. of carbonic dioxide and 0.0584 gr. of water.
II. 0.2049 gr. of the substance gave 16.2 c. c. of nitrogen at a temperature of 17°.5 and a pressure of 763.7 mm.
III. 0.2044 gr. of the substance gave according to the method of Carius 0.0836 gr. of argentic bromide.
IV. 0.2272 gr. of the substance gave 0.0930 gr. of argentic bromide.

	Calculated for $C_6HBr(NO_2)_3COH(CO_2C_2H_5)_2$.	Found.			
		I.	II.	III.	IV.
Carbon	33.47	33.28			
Hydrogen	2.58	3.33			
Nitrogen	9.02		9.20		
Bromine	17.17			17.41	17.42

Our reasons for considering this a tartronic ester rather than a phenol have been given already in the introduction to this paper. The yield is satisfactory, considering the amount of loss to be expected from such a method of preparation; 1 gr. of bromtrinitrophenylmalonic ester gave 0.4 gr. of the substance, or about 40 per cent of the theoretical yield.

Properties. — The bromtrinitrophenyltartronic ester crystallizes from alcohol in long white prisms, terminated by planes at a very obtuse angle to each other, so that the ends look almost but not quite square. These crystals are often arranged in radiating groups, and in that case are generally much more slender than when occurring in isolated prisms. It is deposited from its solution in hot nitric acid in rather sharp slender needles. It melts at 156°, and is nearly but not quite insoluble in water, whether hot or cold; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; freely soluble in benzol, glacial acetic acid, or acetone; soluble in ether, and somewhat more so in chloroform; nearly insoluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is hot alcohol. Strong sulphuric acid has no action upon it in the cold, but if hot, dissolves it with difficulty with a reddish brown color; strong hydrochloric acid has no action on it hot or cold in open vessels, but decomposes it if the two substances are heated together in a sealed tube; nothing could be obtained from the products, however, except a mass like a dry varnish, which we did not succeed in bringing into a state fit for analysis. An exactly similar result was obtained in an attempt to saponify it with sulphuric acid of specific gravity 1.44. Strong nitric acid has no action on it at first, whether cold or hot, but if heated with it for some time seems to destroy it completely, and a similar result was obtained upon boiling it with bromine and water, as in both these cases we could not succeed in isolating any organic oxidation product.

Acid sodic carbonate in aqueous solution had no action on bromtrinitrophenyltartronic ester, but on the addition of alcohol a pale red color appeared, which became more marked on standing; potassic carbonate also did not affect it in aqueous solution, but gave a strong dark red solution on addition of alcohol; aqueous sodic hydrate turned the crystals brown, and dissolved some of them with a brownish color; on the addition of alcohol all the substance went into solution with a dark red color; ammonic hydrate gave a red solution, but the action was not complete until alcohol was added, when the solution became very dark red. The bromtrinitrophenyltartronic ester therefore showed the strong acid character which we should expect, but no attempt was made to analyze its salts, as it was found that the bromine atom was removed by alkaline solutions with great ease, sodic bromide being formed, when it was treated with sodic ethylate even in the cold.

Anilidotrinitrophenyltartronic Ester, $C_6H(C_6H_5NH)(NO_2)_3COH(COOC_2H_5)_2$.

This substance was made by adding an excess of aniline to solid bromtrinitrophenyltartronic ester: the reaction ran smoothly with a slight evolution of heat, and was complete after the mixture had been allowed to stand for a few minutes, when the aniline bromide and excess of aniline were removed by washing with very dilute hydrochloric acid, and the bright yellow residue purified by crystallization from alcohol. At first rounded masses of radiating needles looking like little balls of fat of a bright yellow color were obtained, but as the crystallization continued, orange-red prisms began to appear, and increased in quantity until after several recrystallizations the greater part of the substance had been converted into this form. This behavior during crystallization suggested to us that the substance probably occurred in two modifications, which was proved to be the case by the determination of the melting points of the two sorts of crystals, the yellow, after thorough purification, melting at about 122°, the red at 143°. As the substance passes from one form to the other with great ease, many experiments were necessary in order to find methods for obtaining each in a state of purity.

Red Modification of Anilidotrinitrophenyltartronic Ester.

To obtain this form from the crude product of the reaction it was crystallized several times from alcohol, until a mixture of the two forms rich in the red had been obtained, and then a strong alcoholic solution of the mixed crystals was allowed to evaporate slowly at temperatures from 50° to 70°. The product thus obtained, which showed no sign of the yellow form, was dried at 100°, and analyzed with the following results: —

I. 0.1792 gr. of the substance gave on combustion 0.3114 gr. of carbonic dioxide and 0.0694 gr. of water.

II. 0.2016 gr. of the substance gave on combustion 0.3534 gr. of carbonic dioxide and 0.0809 gr. of water.

III. 0.1938 gr. of the substance gave 19.9 c. c. of nitrogen at a temperature of 22° and a pressure of 767.7 mm.

	Calculated for	Found.		
	$C_6H(C_6H_5NH)(NO_2)_3COH(CO_2C_2H_5)_2$.	I.	II.	III.
Carbon	47.69	47.40	47.80	
Hydrogen	3.77	4.30	4.46	
Nitrogen	11.71			11.76

The air-dried red crystals lost only 0.19 per cent when dried at 100°, and therefore were free from water or alcohol of crystallization.

Properties. — The red form of anilidotrinitrophenyltartronic ester crystallizes in well formed prisms, often half a centimeter long, with at each end a pyramidal termination consisting of four planes. It has an orange-red color like that of potassic dichromate, and melts at 143°; is essentially insoluble in cold water, very slightly soluble in boiling water, forming a pale yellowish solution; soluble in cold alcohol, rather freely in hot. This solution if allowed to evaporate at temperatures from 50° to 70° deposits crystals of the red modification, as has been already stated; but if allowed to evaporate at ordinary temperatures, a mixture of red and yellow crystals is usually obtained, although occasionally only red crystals are formed under these conditions. The red modification is more soluble in methyl than ethyl alcohol; very freely in acetone. Both these solutions deposit some yellow crystals. Soluble in ether or chloroform: slightly soluble in cold benzol, freely in hot. The solution in benzol or chloroform deposits the substance in a viscous state. It is slightly soluble in cold glacial acetic acid, more soluble in hot; from this solution it is usually precipitated by the addition of water in the yellow form, although once or twice we thought we obtained the red modification; very slightly soluble in carbonic disulphide; insoluble in ligroine. Strong sulphuric acid when cold has no action on it, but dissolves it with a brownish yellow color when hot; strong nitric acid dissolves it partially when cold with a yellow color, and the action is increased by heating; cold hydrochloric acid has no action on it, but dissolves it very slightly when hot.

Yellow Modification of Anilidotrinitrophenyltartronic Ester.

This substance was most conveniently obtained from the mixture of the two forms, after it had been purified by several crystallizations from alcohol, by dissolving it in warm glacial acetic acid, and, after allowing the solution to stand for some hours, precipitating the solid matter by the addition of water. The yellow powder thus obtained was dried at ordinary temperatures over sulphuric acid, and analyzed with the following results: —

I. 0.1879 gr. of the substance gave on combustion 0.3284 gr. of carbonic dioxide and 0.0726 gr. of water.

II. 0.1924 gr. of the substance gave 20.5 c. c. of nitrogen at a temperature of 25° and a pressure of 769.7 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3COH(CO_2C_2H_5)_2$.	Found.	
		I	II.
Carbon	47.69	47.66	
Hydrogen	3.77	4.29	
Nitrogen	11.71		12.05

The substance dried over sulphuric acid lost no weight when heated to 100°, showing that it contains neither water nor alcohol of crystallization.

Properties. — The yellow form crystallizes in very fine needles united into spherical groups like those of wavellite, looking frequently like little balls of fat, and has a full yellow color like that of potassic chromate. It is hard to determine the melting point with accuracy, because this form is quickly changed into the red modification, at least in part, when heated to a few degrees below that temperature; it is necessary therefore to heat the bath up to the melting point before immersing the capillary tube containing the substance; under these conditions it melts, and then changes to the red form, and solidifies again, after which it does not melt until about 140°. The melting point we ascribe to this substance is 122°, but we are not sure that this is accurate to one degree. This change from yellow to red can also be brought about slowly by heating at 100°, by boiling the yellow form with water for some time, or most conveniently by crystallization from alcohol at temperatures from 50° to 70°. In its solubility in the different solvents the yellow form does not differ much from the red, but seems in general to be more soluble.

We have made many attempts to determine the molecular weights of the two modifications by the method of Raoult, but have not as yet succeeded in finding any solvent which gives satisfactory results. Acetic acid, owing to its conversion of the red into the yellow form, could at best give results only for the latter, but a number of determinations showed us that it was of no use even for this purpose, as results were obtained varying from 295 to 345 (the theoretical molecular weight is 478), therefore showing that some reaction (probably the formation of an acetoxymalonic ester) had taken place between the acetic acid and the ester. An experiment with phenol gave an excellent result with the red form, 477 instead of 478; but with the yellow only 307 was obtained, indicating a chemical action similar to that observed with acetic acid, and we are not inclined to accept any result with phenol, however excellent it may appear, as with a substance which is so easily affected by solution as this there can be no certainty that it has remained in the same modification, unless it can be recovered directly from the solution used, and this we have found no means of doing in the case of phenol. Benzol gives such uncertain results with substances containing a hydroxyl group,* that we did not think it worth while to try it. We have hopes that naphthaline† may give the desired result for the red form; this will be tried in this Laboratory, and a further attempt made to find a satisfactory solvent for the yellow modification; but as the departure of one of us from Cambridge makes it necessary to postpone further work in this direction until next year, we have thought it best to publish at once our present results, which have already reached a certain completeness.

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* Ber. d. ch. G., XXI. 707.

† Ber. d. ch. G., XXII. R. 128.

Salts of Anilidotrinitrotartronic Ester.

The anilidotrinitrotartronic ester has well marked acid properties. An aqueous solution of acid sodic carbonate has essentially no action on it, but if alcohol is added there is a slight but distinct action indicated by the change of color; potassic carbonate gives in aqueous solution a slight red color, which becomes a strong red if alcohol is added; sodic hydrate in aqueous solution gives a very dark red, apparently converting the substance completely into its salt; ammonic hydrate also gives a strong red color, which is intensified on the addition of alcohol. Some of the alkaline salts were studied more carefully with the folfowing results.

Monopotassium Salt, $C_6H(C_6H_5NH)(NO_2)_3COK(COOC_2H_5)_2$.

This salt was made by adding 20 c. c. of absolute alcohol to 0.5 gr. of the ester, and then a large excess of pure potassic carbonate; carbonic dioxide was given off, the solution became very dark red, and after digesting the substances for eight to ten minutes with the occasional aid of a little heat, the dark brown solution was filtered from the excess of potassic carbonate, evaporated to dryness in a beaker sunk throughout its whole length in the steam bath, and analyzed with the following results: —

I. 0.3458 gr. of the salt heated with strong sulphuric acid gave 0.0548 gr. of potassic sulphate.

II. 0.3748 gr. of the salt gave 0.0696 gr. of potassic sulphate.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3COK(CO_2C_2H_5)_2$.	Found.	
		I.	II.
Potassium	7.58	7.11	8.34

The absolute alcohol used in the second analysis had not been freshly prepared, and the slight excess of potassium can be accounted for by the assumption that it had absorbed a little water.

Properties. — The acid potassic anilidotrinitrophenyltartronic ester, when prepared by the method described above, forms a brownish black amorphous solid, freely soluble in water or alcohol, slightly soluble in ether, and insoluble in benzol. The solutions have a dark brown color.

Disodium Salt, $C_6H(C_6H_5NNa)(NO_2)_3CONa(COOC_2H_5)_2$.

This salt seemed to be formed, to our great surprise, by the action of an alcoholic solution of sodic hydrate on an excess of the anilidotrinitrophenyltartronic ester. To prepare it, about 0.7 gr. of the ester were mixed with a little alcohol, and somewhat less than the amount of sodic hydrate (also in alcoholic solution) necessary to form a mono sodium salt; a little ether was then added to the dark red solution, which was evaporated rapidly to dryness, the small beaker containing it being sunk throughout its length in the steam bath. After this the excess of unaltered ester was extracted with benzol, and the salt dried at 100°, and analyzed with the following results: —

I. 0.2596 gr. of the salt gave after evaporation and ignition with sulphuric acid 0.0672 gr. of sodic sulphate.
II. 0.2848 gr. of the salt gave 0.0698 gr. of sodic sulphate.

	Calculated for	Found.	
	$C_6H(C_6H_5NNa)(NO_2)_3CONa(CO_2C_2H_5)_2$.	I.	II.
Sodium	8.81	8.39	7.94

These results agree with the percentage corresponding to the formula as nearly as can be expected, when it is remembered that the salt was not crystallized, or purified in any other way; but still we cannot feel that they do more than make it highly probable that this is the composition of the salt, as it is certainly strange that a neutral salt should have been formed when such an excess of the acid substance was present, and we had no means of proving that the substance analyzed was a pure salt rather than a mixture; in fact, we observed a slight smell of phenylisocyanide during its preparation, indicating a deep decomposition of part of it, — only a very small part, however, if we may judge from the smell.

Properties. — The salt prepared as described above formed a dark reddish brown to black amorphous mass, soluble in water or alcohol; slightly soluble in ether; insoluble in benzol. Its solutions have a brownish red color.

The behavior of a solution of the ammonium salt of anilidotrinitrophenyltartronic ester, made by adding ammonic hydrate to an excess of the ester, although it smelt strongly of ammonia, was tested with various reagents and gave the following characteristic precipitates: —

With a *zinc salt*, orange-brown.
With a *manganese salt*, brown.
With a *cadmium salt*, reddish brown.
With a *copper salt*, yellowish brown.
With a *lead*, *mercuric*, or *silver salt*, reddish brown.

The fact that the ammonium salt gives no precipitate with salts of magnesium, calcium, strontium, or barium, is also highly characteristic.

Although, as has been already stated, no definite results were obtained from our attempts to oxidize or saponify the bromtrinitrophenyltartronic ester, we thought that perhaps the anilido compound might behave better, and accordingly the following experiments were made, in the hope (unfortunately not realized) of decomposing the anilidotrinitrophenyltartronic ester into substances which would confirm our inferences in regard to its nature. The substance was allowed to stand in the cold with an aqueous solution of potassic permanganate, but, although a considerable part of it disappeared, no organic oxidation product could be detected. In the hope of saponifying the ester, we added to it an excess of sodic hydrate dissolved in water, and allowed the reddish brown solution thus formed to stand in a corked flask at ordinary temperatures for some weeks. During this standing a strong odor of phenylisocyanide was developed, and, if the amount of ester was small, the color changed to yellow; if, on the other hand, the quantity was large, it retained its dark brown color; at the end of the experiment, nothing was obtained except a brown precipitate of most unpromising appearance, formed by adding an acid to the solution, and the phenylisocyanide already mentioned as recognized by its smell. As the formation of this substance would necessitate a complete destruction of the benzol ring which carried the nitro groups and malonic ester radical, we did not think it worth while to repeat the experiment.

This formation of an isocyanide from the destruction of a benzol ring containing nitro groups by means of an aqueous solution of sodic hydrate recalls the work of Post and Hübner,* who found that ordinary dinitrobenzol when boiled with a solution of sodic or potassic hydrate was decomposed with formation of a cyanide quickly if the solution was strong, slowly if it was dilute. They also found that picric acid behaved in the same way, thus confirming the earlier observation of Wöhler.†

Anilidotrinitrophenylmalonic Ester,
$C_6H(C_6H_5NH)(NO_2)_3CH(COOC_2H_5)_2$.

This substance was made to see whether it would be possible by treatment with nitric acid to convert it directly into either its nitrite or the anilidotartronic ester described above. It was found, however, that standing for several days at ordinary temperatures with strong nitric acid produced complete decomposition of part of the substance, the only product insoluble in the acid being unaltered anilidotrinitro-

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* Ber. d. ch. G., V. 408 (1872).

† Pogg. Ann., XIII. 488 (1828).

phenylmalonic ester; and that upon heating it on the steam bath with nitric acid for three hours in the hope of making the anilidotrinitrophenyltartronic ester, the substance was destroyed completely, oxalic acid being the only product which we could find. It seems therefore that the less acid anilido compound cannot be converted into the nitrite or tartronic ester. But although these attempts to oxidize the substance have failed, we add the description of the anilidotrinitrophenylmalonic ester, which has not been prepared heretofore.

It is easily made by adding an excess of aniline to solid bromtrinitrophenylmalonic ester. The reaction ran smoothly in the cold with slight evolution of heat, and the product was purified by washing with very dilute hydrochloric acid to remove the excess of aniline and the aniline bromide, and crystallization from alcohol until it showed the constant melting point 133°, when after drying at 100° it was analyzed with the following result: —

0.1866 gr. of the substance gave 20.2 c. c. of nitrogen at a temperature of 25°.5 and a pressure of 764.3 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3CH(CO_2C_2H_5)_2$.	Found.
Nitrogen	12.13	12.12

Properties. — The anilidotrinitrophenylmalonic ester crystallizes in long slender sharp needles arranged in radiating bunches. It has a full yellow color, and melts at 133°. It is very slightly, if at all, soluble in cold water, more soluble in hot, as shown by the faint yellow color of the solution; freely soluble in hot alcohol, less so in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in chloroform; freely in benzol or acetone; soluble in ether, or glacial acetic acid; slightly in carbonic disulphide; insoluble in ligroine. Boiling alcohol is the best solvent for it. Strong sulphuric acid or nitric acid dissolves it slightly in the cold with a yellow color; the solubility is somewhat increased by heating; strong hydrochloric acid acts on it only very slightly, cold or hot. An aqueous solution of acid sodic carbonate has no action upon it, but there is a barely perceptible change of color if alcohol is added; aqueous potassic carbonate gives little if any action, but on the addition of alcohol a brown solution is formed, the action however seems to be incomplete; aqueous sodic hydrate turns the crystals dark and brown, the solution becoming yellow, the addition of alcohol seems to convert the substance completely into the sodium salt; aqueous ammonic hydrate gives a barely perceptible yellow color, which is not increased by the addition of a little alcohol, but a large amount gives a dark brown solution.

A solution of the sodium salt of anilidotrinitrophenylmalonic ester made by adding a drop of sodic hydrate to an excess of the ester moistened with alcohol, and then diluting largely with water, gave characteristic precipitates with the following reagents: —

With a *calcium salt*, a heavy reddish brown precipitate.

With a *strontium salt*, a slighter precipitate.

With a *barium salt*, a very faint precipitate.

A *magnesium salt* gives a reddish brown precipitate, as heavy as that obtained with the calcium salt.

With a *manganese salt*, reddish brown flocks.

With a *zinc salt*, yellowish brown.

With a *cadmium salt*, orange-yellow.

With a *copper salt*, yellowish brown.

With a *lead salt*, reddish brown.

With a *silver salt*, dark reddish brown.

Its most striking property is that the barium salt is the most, the calcium salt the least, soluble of its salts with metals of the second group, and in this respect it resembles its mother substance, the bromtrinitrophenylmalonic ester,[*] the corresponding acetacetic ester,[†] and the orthonitrobenzoylmalonic ester of Bischoff.[‡]

Nitrite of Trinitrophenylenedimalonic Ester,
$C_6H(NO_2)_3CH(COOC_2H_5)_2CNO_2(COOC_2H_5)_2$.

After we had studied the action of nitric acid on the bromtrinitrophenylmalonic ester, it seemed of interest to determine whether the dimalonic compound acted in the same way, and accordingly we proceeded as follows. A small quantity of the trinitrophenylenedimalonic ester[§] (melting-point 123°) was covered with nitric acid of specific gravity 1.38, and warmed in a dish on the steam bath for two minutes; the solid turned dark yellow, and melted to a drop of oil. The acid was then allowed to cool, poured off, and replaced by the same quantity of fresh acid, when it was warmed as before for three minutes, making five in all. Upon standing, the oily product solidified to a mass of crystals, which were washed thoroughly with water, and at first recrystallized from alcohol; but as in each crystallization a small quantity of yellow oil was formed, we feared a partial decomposition, and resorted to the method which had given excellent results in the purification of the nitrite of bromtrinitrophenylmalonic ester, that is,

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[*] These Proceedings, XXIV. 261.

[†] Ibid., 278.

[‡] Ann. Chem., CCLI. 362.

[§] These Proceedings, XXIV. 268.

dissolving the substance with very little heat in chloroform, and then adding enough alcohol to start the separation of crystals; in this way a pure substance melting at 111° was obtained without difficulty, which was dried at about 70° and analyzed with the following results: —

I. 0.1960 gr. of the substance gave on combustion 0.3012 gr. of carbonic dioxide and 0.0714 gr. of water.

II. 0.1926 gr. of the substance gave 16.7 c. c. of nitrogen at a temperature of 23° and a pressure of 771 mm.

	Calculated for $C_6H(NO_2)_3CH(CO_2C_2H_5)_2CNO_2(CO_2C_2H_5)_2$.	Found I.	Found II.
Carbon	41.81	41.91	
Hydrogen	3.83	4.05	
Nitrogen	9.76		9.93

The substance is therefore the mononitrite of trinitrophenylenedimalonic ester.

Properties. — The substance crystallizes in rather thick plates with parallel sides terminated at each end by two planes at an acute angle to each other, these acute angles being usually, but not always, truncated by planes at right angles to the parallel sides. The crystals are often much twinned and grouped into very irregular forms. It has a lemon-yellow color, and melts without decomposition at 111°. It is very slightly soluble in boiling water, giving a pale yellow solution, essentially insoluble in cold; slightly soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; both these solvents seem to produce a slight decomposition of the substance when heated with it; very freely soluble in chloroform; freely soluble in benzol, or acetone; soluble in ether, or glacial acetic acid; slightly soluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol used as described above. Strong sulphuric acid has no action on it in the cold, but, when heated with it, dissolves some of it with a pale yellow color after it melts; strong hydrochloric acid has no apparent action on it either hot or cold; strong nitric acid has no action on it in the cold, but dissolves it slightly when hot, and if heated with it for two hours and a half destroys it completely, the only product which we isolated being oxalic acid; on one occasion, however, another product melting near 140° was obtained in small quantity, but we did not feel sufficiently interested in this part of the subject to prepare enough of it to determine whether it was the dinitrite or a tartronic ester. One thing, however, these experiments have established, namely, that the dimalonic compound is less stable toward nitric acid than the brommalonic compound, since the latter, after three hours' boiling with the acid, had not gone further than the tartronic ester, while the former usually underwent a total decomposition. On the other hand, the nitrite of the dimalonic compound is not decomposed by melting, and only slightly by heating with alcohol, and therefore in these two respects is more stable than the nitrite of bromtrinitrophenylmalonic ester.

The nitrite of trinitrophenylenedimalonic ester shows acid properties. With an aqueous solution of acid sodic carbonate it gives no action, and very little when alcohol is added, unless in very large quantity, when a yellowish solution is formed; with potassic carbonate in aqueous solution there is no action, but on the addition of alcohol a very strong yellowish brown color; aqueous sodic hydrate gives a reddish solution, on the addition of alcohol an orange flame-colored solution, entirely different in color from that given with the potassic carbonate; ammonic hydrate imparts a strong yellow coloration to the solution, intensified on the addition of alcohol. Upon comparing the acidity of this substance with that of the trinitrophenylenedimalonic ester, it seems as if this latter substance were somewhat more acid than the nitrite, since it gives a slight coloration with aqueous potassic carbonate, and seems to act more easily with acid sodic carbonate and alcohol, but the difference between the two in this respect is certainly very slight, which we should not have expected, as it seemed probable that the introduction of the nitrous acid radical (ONO) would have increased the ease with which the hydrogen in the other malonic ester radical was removed.

A solution of the sodium salt of the nitrite of trinitrophenylenedimalonic ester was made by adding one drop of sodic hydrate solution to a large excess of the ester moistened with alcohol, and, after the action had taken place, diluting with much water. The solution thus obtained was of the color of a solution of potassic dichromate, but much less strongly colored than the solutions of the salts of any of the related substances. Its action with the various reagents was tried, and the following characteristic precipitates observed: —

With *barium salt*, rather heavy yellow flocks.

With *mercurous* or *lead salts*, heavy yellow flocks.

With *silver* or *copper salts*, yellow flocks.

Salts of *calcium*, *strontium*, or *magnesium* gave only faint yellow precipitates, decidedly different from the heavy one produced by baric chloride.

Nitrite of Bromdinitrophenylmalonic Ester, $C_6H_2Br(NO_2)_2CNO_2(COOC_2H_5)_2$.

Although bromdinitrophenylmalonic ester does not change in color when heated with nitric acid, as has been stated more than once in previous papers* from this Laboratory, it really is affected in the same way as the corresponding trinitro compound, being converted into its nitrite, but without the formation of the red secondary product which made the reaction so striking in that case. The substance was prepared as follows. A small quantity of the bromdinitrophenylmalonic ester (melting point 75°–76°) was heated on the steam bath with nitric acid of specific gravity 1.38 for five minutes, or longer (as the same compound was obtained if the heating was continued three hours); there was at first no sign of a reaction except a slight evolution of nitrous fumes; but, as the heating continued, the undissolved solid melted, forming an oil drop, which after cooling solidified to a mass of crystals, while at the same time the acid liquid deposited crystals looking very much like those of the bromtrinitrophenyltartronic ester. All of these crystals were purified by recrystallization from boiling alcohol, until they showed the constant melting point 111°, when they were dried at about 70°, and analyzed with the following results: —

I. 0.1973 gr. of the substance gave on combustion 0.2492 gr. of carbonic dioxide and 0.0510 gr. of water.

II. 0.2084 gr. of the substance gave 17.4 c.c. of nitrogen at a temperature of 22° and a pressure of 755.6 mm.

	Calculated for $C_6H_2Br(NO_2)_2CNO_2(CO_2C_2H_5)_2$.	Found I.	Found II.
Carbon	34.66	34.44	
Hydrogen	2.67	2.87	
Nitrogen	9.33		9.41

The substance therefore is the nitrite of the bromdinitrophenylmalonic ester, and not the corresponding tartronic ester, as we had expected from the long heating used in one of the methods of preparation, and from the fact that no difficulty was encountered in making the combustion of it.

Properties. — The nitrite of bromdinitrophenylmalonic ester crystallizes usually in thick rhombic crystal often one millimeter in each direction, which look somewhat like rhombohedra with a sharp acute angle, but are seen to be twins by the lines of twinning and stria-

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* These Proceedings, XXIV. 6, 257.

tions; the obtuse angles on these crystals are often truncated. Less commonly with the characteristic forms just described, long flattened prisms occur, which are terminated by a single plane at a sharp acute angle, rarely by two. It is easy to see that the rhombic crystals could be formed by the twinning of these prisms. The crystals are very lustrous, of a white color, with a slight greenish cast, and melt at 111° without decomposition. The substance is essentially insoluble in cold water, very slightly soluble in hot; soluble in cold alcohol, more so, but still far from freely, in hot. It shows no signs of decomposition when boiled with alcohol. It is more soluble in methyl than in ethyl alcohol, cold or hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in ether or carbonic disulphide; nearly, if not quite, insoluble in ligroine. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when hot dissolves a little of the substance after it has melted; strong hydrochloric acid has no action, hot or cold; strong nitric acid has no action on it in the cold, but when hot dissolves a little of it, which is deposited on cooling. Neither acid sodic carbonate nor neutral potassic carbonate had any action with it, even in presence of alcohol; sodic hydrate in aqueous solution was without action; if alcohol was added, a portion of the substance dissolved slowly with a yellow color, but most of the white crystals were left unattacked; ammonic hydrate in aqueous solution had no action, with alcohol little or none. The substance behaves, therefore, as we should expect, a salt being formed only by a reagent like sodic hydrate strong enough to remove the NO_2 group attached to the side-chain

The nitrite of bromdinitrophenylmalonic ester is much more stable than the corresponding trinitro compound, since it is not decomposed by boiling with alcohol, or at its melting point, or by boiling with nitric acid; for, as has been already stated, it could be made by boiling for three hours with nitric acid, whereas under these conditions the trinitro compound was converted into the tartronic ester. Nor did longer boiling of the dinitro compound with nitric acid produce the tartronic ester, as even after seven hours it showed the melting point of the unaltered substance 111°. As the trinitro tartronic ester had been obtained also by heating the corresponding nitrite, we tried the same experiment with the dinitro nitrite, and found that, when heated a few degrees above its melting point, it turned rather dark colored, and gave off bubbles of gas, in which bromine was recognized by the smell. The residue was oily, but after solution in alcohol crystals were obtained which showed the characteristic rhombic form of the nitrite of bromdinitrophenylmalonic ester. This experiment therefore seemed to show that the action of heat consisted only in the complete decomposition of a portion of the nitrite of bromdinitrophenylmalonic ester, and, as it did not promise to give the desired tartronic ester, further work in this direction was abandoned.

Reduction of the Nitrite of Bromdinitrophenylmalonic Ester.

The conversion of the nitrite of bromtrinitrophenylmalonic ester into the corresponding tartronic ester by nitric acid, or by the action of heat, indicates that the group NO_2 in the side-chain is attached to the molecule by oxygen instead of nitrogen, or, in other words, that the substance is a nitrite, and not a nitro compound; but, as we could not consider this a conclusive proof of the oxygen attachment, we have studied the reduction of a body of this class, selecting for this purpose the dinitro compound, because it is more easily prepared than the corresponding substance containing three nitro groups, and also because the product obtained from it by reduction would probably be more stable than one containing one more amido group.

Six grams of the nitrite of bromdinitrophenylmalonic ester divided into three lots of two grams each were mixed with granulated tin, strong hydrochloric acid, and a few drops of alcohol, and after adding a piece of platinum to accelerate the reaction, were allowed to stand on a steam radiator (50°–70°) until all the organic matter had dissolved, and no further action was observed, which happened usually in about an hour and a half. If quantities larger than two grams were used a very dark colored solution was obtained. The solution poured off from the excess of tin was freed from stannous and stannic chlorides by means of sulphuretted hydrogen, when a residue was obtained by evaporation of the filtrate, which gave off ammonia gas when treated with an alkaline hydrate, and formed a precipitate of ammonic chlorplatinate with chlorplatinic acid; it evidently therefore contained ammonic chloride in addition to the chloride of the organic base. The washings of the sulphide of tin, which were worked up separately from the filtrate, on the other hand, yielded crystals which showed only a very slight amount of ammonic chloride by the same tests, and accordingly these crystals were dried at 100°, and analyzed with the following results: —

I. 0.1980 gr. of the substance gave 25.25 c. c. of nitrogen at a temperature of 23° and a pressure of 764.8 mm.

II. 0.1954 gr. of the substance gave by the method of Carius 0.1480 gr. of argentic chloride.

	Calculated for $C_6H_3NH_3Cl(CHOHCONH)$.	Found. I.	 II.
Nitrogen	13.96	14 47	
Chlorine	17.70		18.73

These results are not all that we could wish; but although they show the presence of the small amount of ammonic chloride, which we had detected by the qualitative tests, they leave no doubt in regard to the composition of the organic substance, and therefore we have not thought it worth while to spend the great amount of time which would have been necessary to prepare a sample entirely free from ammonic chloride; especially as these analyses prove that the group NO_2 is attached to the side-chain by oxygen, since we obtained, by the reduction of the nitrite of bromdinitrophenylmalonic ester, ammonic chloride and the chloride of amidoxyoxindol instead of the chloride of diamidoxindol, which would have been formed if the group NO_2 had been attached to the molecule by the nitrogen.

Properties of the Chloride of the Amidoxyoxindol, $C_6H_3NH_3Cl(CHOHCONH)$.

This substance was obtained crystallized in rather large plates, usually in forms like a closed fan terminated by an obtuse angle, and set in rows one over the other with the obtuse angles parallel, or arranged in branching arborescent forms like coral; sometimes in thicker sharp prisms. It had a dark yellow color as we observed it; was soluble in cold water, more so in hot; slightly soluble in cold or hot alcohol, and insoluble, or nearly so, in most of the other solvents. The strong acids gave no striking reactions with it, except strong nitric acid, which turned it orange-red; but this seemed to be due to some nitrous acid in the nitric, as on the addition of sodic nitrite the color was much intensified. Sodic hydrate added to the aqueous solution gave a few brown flocks, evidently from decomposition of a part of the base; ammonic hydrate gave a tolerably heavy flocculent precipitate, at first whitish, but turning brown on exposure to the air, but it showed no signs of crystallization, and with the small amount of substance at our disposal we have been unable to obtain the free base in any definite form. The chloride mixed with alcohol and some strong hydrochloric acid imparted after some time a dark red color to a piece of pine wood.

Attempt to make Dinitrophenylenedimalonic Ester.

The results just described having shown that the behavior of bromdinitrophenylmalonic ester toward nitric acid was not so different from that of the trinitro compound as we had at first supposed, it became of interest to determine whether other apparent differences between these two bodies were no better marked, and accordingly we tried to make the dinitrophenylenedimalonic ester by the method which had given good results with the trinitro compound as follows: — 3 gr. of bromdinitrophenylmalonic ester were dissolved in ether, and, after the addition of 1.5 gr. of malonic ester previously treated with 0.15 gr. of sodium in a large quantity of alcohol, the mixture was boiled under a return-condenser for three hours; at the end of this time the solution had turned deep red, and a little solid had separated. The product was treated with water and dilute sulphuric acid, the ether separated, and the aqueous liquid tested for sodic bromide, which it was found to contain in small quantity, but the crystals deposited by the ether melted after one crystallization at 75°–76°, the melting point of bromdinitrophenylmalonic ester. We infer from this experiment, therefore, that, although a little dinitrophenylenedimalonic ester may have been formed, its quantity was exceedingly small, and that the reaction, if it goes on at all, certainly takes place with much more difficulty in the case of the dinitro than in that of the trinitro compound.

VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

NOTE ON TRIBROMMONONITROBENZOL.

By C. Loring Jackson and W. B. Bentley.

Presented May 13, 1891.

The results of experiments on the behavior of tribromtrinitrobenzol and tribromdinitrobenzol with various reagents have been described in a number of papers from this Laboratory. For the sake of completeness, we felt it necessary to include the tribrommononitrobenzol in our investigation, and were the more inclined to do this as we hoped that it might throw some light on the replacement of bromine by hydrogen, so often observed in our work with the trinitro and dinitro compounds. This hope has not, however, been fulfilled, as no such replacement of bromine by hydrogen was observed, and the tribrommononitrobenzol has proved to be so inert with various reagents, that it deserves only the short investigation the results of which are given in this paper.

The tribrommononitrobenzol used in this work was prepared by boiling symmetrical tribrombenzol (melting point 119°) for fifteen minutes with a nitric acid made by adding to fuming nitric acid (specific gravity 1.51) one quarter of its volume of common strong nitric acid (specific gravity 1.38). The greater part of the tribrommononitrobenzol separated as the mixture cooled, and the rest was obtained by the addition of water to the acid mother liquor. This process gave better results than when acetic acid was used to dilute the fuming nitric acid according to the method given by V. von Richter.*

Action of Tribrommononitrobenzol with Sodic Ethylate.

The tribrommononitrobenzol melting at 125° was acted on by hot sodic ethylate giving a substance which we found it convenient to

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* Ber. d. ch. G., VIII. 1426.

prepare as follows: — 5 gr. of tribrommononitrobenzol dissolved in benzol were mixed with an alcoholic solution of the sodic ethylate from 1 gr. of sodium, heated on the water bath just below boiling for some time, and then allowed to stand at a temperature a little above the ordinary for several hours. The red solution thus obtained was filtered from a precipitate which had formed, (this gave a test for bromide with argentic nitrate,) diluted with water, and acidified with dilute sulphuric acid, after which the benzol was separated from the aqueous liquid; this was extracted with ether, and the combined extracts from the organic solvents purified by crystallization from alcohol until the constant melting point 91° was reached. Sometimes a black tarry product was obtained from the reaction, instead of the white crystals formed if the process had gone well. This tarry mass was worked up most conveniently by distillation with steam, followed by crystallization of the steam distillate from alcohol. The pure substance was dried at about 70°, and analyzed with the following results: —

I. 0.1900 gr. of the substance gave by the method of Carius 0.2181 gr. of argentic bromide.

II. 0.3800 gr. of the substance gave 15.9 c. c. of nitrogen at a temperature of 22° and a pressure of 756.5 mm.

	Calculated for $C_6H_2Br_2NO_2OC_2H_5$.	Found. I	Found. II.
Bromine	49.22	48.85	
Nitrogen	4.31		4.72

The substance is therefore dibromnitrophenetol, and was formed by the replacement of one atom of bromine by the ethoxy radical.

Properties. — The dibromnitrophenetol crystallizes in bundles of prisms, which are usually somewhat flattened and terminated by a basal plane, also occasionally showing with this two other planes at an obtuse angle to each other. It is white, but turns brown on exposure to the air; melting point 91°; essentially insoluble in cold water, perhaps very slightly soluble in hot; alcohol disolves it sparingly when cold, freely when hot; more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, acetone, or carbonic disulphide; freely soluble in ether; slightly soluble in cold glacial acetic acid, soluble in hot; very slightly soluble in ligroine. The best solvent for it is hot alcohol. It distils with steam. Strong sulphuric acid has no action in the cold, but when hot gradually forms a black solution; cold nitric acid has no action on it, but when hot dissolves it, depositing crystals on cooling, which seem by their melting point to be the unaltered substance; strong hydrochloric acid seems to have no action, whether hot or cold; sodic hydrate seems not to act upon it.

Action of other Reagents on Tribrommononitrobenzol.

Sodic methylate behaved in much the same way as the sodic ethylate, except that it was necessary in this case to heat for a longer time, and even after this a certain amount of tribrommononitrobenzol was apt to be left unaltered. The product after crystallization from alcohol showed the constant melting point 104°, but its analyses gave percentages of bromine differing from those corresponding to dibromnitroanisol by about one per cent. The cause of this is probably the same as that of the similar want of agreement between the calculated and observed percentages in the case of the bromdinitroresorcine dimethylether;* but we have not thought the substance of sufficient importance to try to obtain better analytical results, which, to judge by our work on the bromdinitroresorcine dimethylether, would be a matter of great difficulty.

From these experiments it appears that the tribrommononitrobenzol acts with sodic alcoholates less easily than the tribromdinitrobenzol, which is attacked by them in the cold forming the ethers of bromdinitroresorcine, whereas it is necessary to heat the mononitro compound to bring about any action. When the tribromdinitrobenzol is heated with an alcoholate, the third atom of bromine is replaced by hydrogen and an ether of the dinitroresorcine is formed, but we found no trace of any action of this sort with the mononitro compound. It is to be noted, too, that only one atom of bromine is removed from the mononitro, but two from the dinitro compound.

The inertness of tribrommononitrobenzol as compared with the corresponding dinitro compound is made even more evident by the study of the action of aniline upon it. This substance converts tribromdinitrobenzol into trianilidodinitrobenzol, when heated with it for a short time, whereas the corresponding trinitro compound is formed in the cold; from the mononitro substance we were unable to obtain any anilido compound, even after heating for some time to the boiling point of aniline; a little aniline bromide was formed, it is true, but almost all of the tribrommononitrobenzol was recovered unaltered, as recognized by its melting point and very characteristic crystalline form.

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* These Proceedings, XXV. 175.

No better result was obtained with sodium malonic ester, which acts on the dinitro and trinitro compounds in the cold, but even after boiling for some time with the tribrommononitrobenzol yielded only a very small quantity of sodic bromide, while almost all of the tribrommononitrobenzol was recovered unaltered.

IX.

ON A KEPHIR-LIKE YEAST FOUND IN THE UNITED STATES.

By Charles L. Mix.

Presented by Professor W. G. Farlow, May 26, 1891.

A species of yeast which causes alcoholic fermentation of milk is well known in Europe, the attention of the leading scientists having been called to it by Edouard Kern, in an article published during November, 1881, and entitled, "Ueber ein neues Milch-ferment aus dem Kaukasus." In order to give an intelligible description of a similar ferment which exists in the United States, a summary of Kern's paper becomes a necessity.

Kern's milk-ferment is found in the region of the Caucasus Mountains, and so far as is known in no other place. It is called by the Caucasian peasants "kephir," "kiphir," "kiaphir," or "kefir." The country being a mountainous one, agriculture is impossible, so that milk and flesh are the food of the peasants. However, they do not drink their milk fresh, but ferment it, adding to it what are known as "kephir-grains" in the proportion of one volume of the grains to six or seven volumes of milk. The whole is then exposed to the air for twenty-four hours at an ordinary temperature, and shaken frequently. The "ferment-milk" thus formed is poured from the grains and mixed with twice its volume of fresh milk, which it ferments in turn, eliminating a large amount of carbonic acid gas, and forming from ½% to 1% of alcohol. When kephir is made successfully, it is a thick fluid without any very large coagulated clumps, and with a pleasantly acid taste; by longer fermentation it becomes a frothing, foaming, strongly acid drink, like the koumiss of the Steppes.

According to Kern, this ferment is used not only as a drink, but also as a curative for various diseases, with great success, various gastric and pulmonary complaints, it is said, being cured by it. Its reputation, Kern continues, has extended beyond the narrow limits of the mountainous region where it originated, and has already reached many cities of the Caucasian district.

Examined with the eye, the kephir-grains when fresh are found to consist of white, compact, elastic masses, enveloped by a slime, and with a spherical or elliptical contour, varying from 1 mm. to 5 cm. in diameter. The very small grains have a smooth spherical exterior, while the larger ones are provided with outgrowths and furrows, looking more or less like a very small cauliflower. When the grains are dried they assume a yellowish brown color, and shrink a good deal by the loss of water. When examined with the microscope there are found in each grain, whatever its form or size, two different structures, yeast cells and Bacteria. The latter form the mass of the grain in which the yeast cells are embedded.

The yeast cells occur in pairs or rows of cells of all shapes and sizes. Most of them are elliptical or spherical, the former varying from 3.2 μ to 9.6 μ by 3.2 μ to 6.4 μ, the spherical ones varying from 3.2 μ to 6.4 μ in diameter. Each yeast cell has a plainly visible membrane with a double contour, brought out by stains. Within the cell is a vacuole, at the poles of which are often found small fat globules in no definite number, but which increase in number as the cell is dried, the protoplasm at the same time becoming granular, the vacuoles diminishing in size and ultimately disappearing. The yeast cells increase by budding.

Kern discusses the question of the possibility that the yeast cells may be the spores of some *Mucor*, as *M. racemosus* for example, since these are known to cause alcoholic fermentation; but since cultures continued for weeks failed to show him a trace of mycelium, he concludes that there can be no doubt that these are true yeast cells.

The origin of the kephir grains was unknown to Kern. He could find no wild form of yeast from which they might have been cultivated; nor could he gather any information as to their source from the peasants. They are said to grow in little clumps or granules on peculiar bushes found on the mountains just beneath the snow line.

Kern could not induce the kephir yeast to form spores. He explains the matter by saying that these yeast cells have for an infinity of generations grown in milk only, and have increased only by budding. Hence, when they are exposed to conditions favorable for spore formation, they are unable to form spores. He declares the kephir yeast to be ordinary *Saccharomyces cerevisiæ*, Meyen, saying that he cannot agree with Dr. Max Reess in classifying yeasts according to their form and size. The form and size of the cells vary too much; besides, the variations are not constant, being conditioned partly by age, partly by the nature of the nourishing medium, and partly by the temperature.

The other portion of the kephir-grain is made up of Bacteria embedded in a zoöglœa mass which is firm and elastic, comprising the bulk of the grain. The individual cells are short, cylindrical, and rod-shaped, 3.2 μ to 8 μ long and 0.8 μ broad, with homogeneous protoplasm. These cells increase by the regular splitting process characteristic of *Schizomycetes.*

The Bacteria in the zoöglœa are motionless; but in addition to these, when the kephir grain is placed in a nutrient solution, there are to be seen moving cells, exactly like the motionless ones in both form and size. By allowing these moving cells to dry upon a slide, then staining with *Extract Campech.* and removing the excess of the stain, Kern was able to demonstrate a very thin thread-like wavy cilium on but one of the ends of each cell.

Exposed to unfavorable conditions the Bacteria cells grow out into Leptothrix threads, varying from 10 μ to 40 μ in length, which are merely the necessary consequences of successive cell-division in which the products do not separate from each other. At various intervals in the length of such a thread agglomerations of protoplasm occur. At first there is hardly an indication of the splitting of such a mass, there being merely tiny incisions on either side; but these become larger and larger, until finally a single protoplasmic mass has given rise to two spores, separated by a regular cell wall. Thus it happens that in a Leptothrix thread each cell has two spores situated one at either end. Kern mentions still another kind of spore formation, seen in the individual cells, which differs markedly from that just described. In these cells spore formation begins with the appearance of a small bright point at each end of the cell. The points enlarge more and more, assume a well defined contour, and ultimately become true spores. The form is always round, the diameter never exceeding that of the mother cell before they are freed, but reaching 1 μ after liberation.

Kern names his kephir Bacterium *Dispora Caucasica*, nov. gen. et nov. sp., with the following distinguishing characteristics: —

(1.) The vegetative cells are in the form of short cylindrical rods, 3.2 μ to 8 μ long, and 0.8 μ broad.

(2.) In the zoöglœa condition the cells form white elastic clumps of considerable size.

(3.) The moving vegetative cells have on *one* end a thin, thread-like, wavy cilium.

(4.) The spores are round; when in the cells their diameter never exceeds that of the mother cell; when free, they may reach 1 μ in diameter.

(5.) The round spores are always two in number, one at each end of the cell.

From this subject Kern passes to his last topic, the power of resistance of the kephir-grains when subjected to external influences. Drying does not seem to deprive them of life. They contract a great deal, become dirty brown and hard as stone, so that they have even been called "little stones" or "pebbles" by the inhabitants of the Caucasus district. In this dried state they are kept for long periods of time, yet under suitable conditions they are always ready to cause fermentation again. Kern himself kept some for two months in his room. They were thoroughly desiccated, yet when placed in milk again they became gradually white, and in a few days could not be distinguished from fresh specimens. Under the microscope the dried clumps show that the yeast cells suffer most, very many being dead; the Bacteria seem to suffer very little, since they form spores.

Having thus summarized Kern's paper rather fully because it bears directly upon my subject, I am in position to describe an American milk-ferment which I hope to show is almost, if not quite, identical with the European kephir. The material which I studied consisted of two sets of specimens placed in my hands by Professor Farlow of Harvard University, to whom they had been sent by Dr. George Thurber, of Passaic, N. J., and Mr. J. Dearness, of London, Ontario. In both cases the specimens were in the form of rather small granules, very few being above a centimeter in diameter, of a dirty brown color, and presenting on their surfaces numerous lobes and fissures, thus reminding one of rather dirty gum-arabic. The material from Dr. Thurber was received in 1888, and at that time had already lain in a dried condition in his herbarium for several years. The specimens from Mr. Dearness, undistinguishable to the naked eye from those of Dr. Thurber, were received in January, 1891, under the name of "California bees' beer," with the note that "housekeepers through this country (Ontario) keep a self-sealing jar of this Saccharomycete half filled or more with sweetened water. The fermented product is drawn and drunk for a tonic."

The material from New Jersey and that from Ontario were practically identical in gross and microscopic characters, the Ontario grains being as a rule somewhat smaller, and the following description applies to both of them. In my experiments on the action in fermentation I used principally the New Jersey material, which, in spite of the long time it had been dried, revived when placed in a nutritive fluid.

I experimented with the Ontario material so far as to make sure that, like the New Jersey form, it caused a fermentation of saccharose; but in studying the fermentation of other sugars I used only the New Jersey form.

When soaked for a time in water, the grains become whitish, very firm and compact, and quite elastic. Examination under the microscope shows them to consist of two elements, a small proportion of yeast cells embedded in zoöglœa masses of rod-shaped Bacteria.

Although in the dried specimens the yeast cells seem entirely dead, yet when placed in a nutrient solution they begin to grow vigorously. They vary in size and shape, from elliptical to spherical, the average diameter of the latter being 4.2 μ, and the former varying from 10.5 μ to 6.5 μ by 6 μ to 4 μ. On careful examination, each yeast cell is found to have a plainly marked double contour, within which is an almost homogeneous protoplasm containing a small vacuole. Cultivation of the yeast cells in water increases the size of the vacuoles, and causes the formation of small fat globules at the poles; and cultivation in strong solutions of saccharose produces two or even three vacuoles in each cell, together with numerous fat globules. When such cells are mounted in a mixture of acetic acid and glycerine, the vacuoles disappear, and the protoplasm becomes finely granular.

The yeast cells increase by budding, growing best in solutions of dextrose and in milk, both of which they ferment; and it is in these substances that the best colonies are to be found. In pure water, the yeast cells for a short time increase slowly in numbers by budding, but no colonies are met with since the daughter cell separates from the mother cell as soon as it is formed. In cane-sugar or saccharose solutions, which the yeast is unable to ferment, the cells increase very rapidly in numbers, but it is hard to find a colony of more than three cells; whereas in milk and in solution of dextrose, colonies numbering at least from ten to fifteen cells are very common.

It was impossible to induce spore formation; and indeed the very fact that the yeast cells gave rise to new cells by the simple process of budding after they had been dried for several months seems to warrant the conclusion that there is no spore formation. That they are yeast cells, and not spores of *Mucor racemosus* or any other *Mucor*, is shown by the fact that not a particle of mycelium was found during the three months in which the yeast was under observation.

Kern decided his yeast to be a form of *Saccharomyces cerevisiæ*, Meyen. In the case of the North American kephir, the species evidently is not *S. cerevisiæ*, however much it resembles that species in general appearance, for it cannot invert cane-sugar as ordinary beer yeast should do. Although I cultivated it in saccharose solutions of all strengths, it never caused a trace of fermentation. As soon, however, as I placed the yeast in a grape-sugar solution, i. e. a solution of dextrose, fermentation ensued. Unfortunately, Kern did not try the effect of his yeast upon saccharose, and we are therefore unable to compare his yeast with that found in American kephir in this important point. But the absence of information can hardly be urged as an evidence that the two forms are not the same. Again, ordinary beer yeast forms spores, while the kephir yeast does not, thus affording another reason for regarding them as distinct species.

Beyerinck has described the yeast which occurs in the Caucasian kephir grain in the "Centralblatt für Bakteriologie," Vol. VI. page 44, naming it *Saccharomyces kefyr* with the following distinguishing characteristics: —

(1.) The cells are of various sizes and shapes, from spherical to elliptical, the former measuring from 3.2 μ to 6.4 μ in diameter, and the latter varying from 3.2 μ – 9.6 μ in the major axis to 3.2 μ – 6.4 μ in the minor.

(2.) The yeast is associated with a rod-shaped Bacterium in a granular mass.

(3.) The yeast is not able to ferment saccharose or cane-sugar.

(4.) It is able to ferment lactose or milk-sugar.

(5.) It has no known spore formation. Since the North American yeast agrees with all these characteristics, while it differs in an important point from *S. cerevisiæ*, it will be sufficient for the present purpose if I apply the name *S. kefyr* to our American form without attempting to discuss at length disputed points in synonymy.

Let us turn now to the Bacteria. The cells are short cylindrical rods with homogeneous protoplasm, varying from 8.5 μ to 4.5 μ long by 0.8 μ broad; precisely agreeing with Kern's measurements. The cells increase by splitting perpendicularly to the long axis, the resulting cells being sometimes joined together, thus producing Leptothrix-like threads of all lengths, even to 120 μ, and sometimes completely separated. Many of the isolated cells possess the power of motion, but after repeated efforts I was unable to demonstrate the presence of cilia.

It is not such an easy matter to induce these cells to form spores as Kern implies that it was in the case of his Bacteria. The best method is to place a clump of the yeast in a watch-crystal with a little water, covering the whole with another crystal. In twenty-four hours

Leptothrix threads, which seem to precede spore formation, begin to form, and within thirty-six to forty-eight hours the spores appear. It will be remembered that Kern gives two distinct methods of spore formation, — one occurring in isolated cells, and the other in the Leptothrix threads. It is no wonder, therefore, that neither method has received general credence. My investigations on the North American form have led to results diametrically opposed to those of Kern. First, I found but one method of spore formation; secondly, I found this method occurring only in the Leptothrix threads, although I sometimes found isolated cells bent or curled in such a manner that spore formation was well simulated. Spore formation in the Leptothrix threads takes place as follows. At each end of every cell of the thread a small bright dot appears, which becomes brighter, larger, and much more highly refractive than the rest of the cell, until finally it assumes a well defined spore wall and develops into a mature spore. Each cell has therefore two spores, one at each end, and each originating independently of the other. In no case did I see two spores formed, as Kern states, by the division of a single agglomerated mass of protoplasm into two portions.

There are two or three other important points in which the American alcoholic milk-ferment closely resembles the Caucasian kephir. So far as I know, no one has ever tried the experiment of making the North American yeast cause the alcoholic fermentation of milk. Struck with its gross and microscopic resemblances to kephir, I was induced to try the experiment, and to my pleasure I obtained alcoholic fermentation, the evolution of carbonic acid gas being sufficient to force the cork from the flask. I easily obtained a large precipitate of $CaCO_3$ from lime-water by the usual test for carbonic acid gas. The presence of alcohol was proved by the iodiform test. Since ethyl alcohol, C_2H_5OH, cannot be detected in the presence of lactic acid, $C_3H_6O_3$, (for lactic acid forms iodiform as easily as ethyl alcohol,) I neutralized with Na_2CO_3 after filtering off the fluid portion of the milk, distilling finally the neutralized filtrate. Thus every trace of lactic acid was removed. With KOH and iodine the distillate gave iodiform, thus proving the presence of alcohol. This fact alone, viz. that this yeast causes alcoholic fermentation of milk, is sufficient to establish a near relation to the Caucasian kephir. Moreover the fermented milk agrees closely with the description of the kephir drink. The milk does not sour in the ordinary sense, for it does not coagulate in large masses; still it is acid, contains some carbonic acid gas and alcohol, and is by no means unpleasant to the taste.

Another way in which this American milk-ferment resembles kephir is, that it causes alcoholic fermentation of dextrose. De Bary is authority for the statement, that the "kephir yeast, like its constituent the Saccharomycete, working by itself, gives rise to alcoholic fermentation in a nutrient solution of grape-sugar, though of a less active kind than that caused by beer-yeast." * The specimen which I had gave a good alcoholic fermentation with dextrose solutions, but caused no fermentation with saccharose. It seems, therefore, to have the power of fermenting only two of our natural sugars, — dextrose and milk-sugar.

When we consider the remarkable similarity of these American grains with the kephir granules in color, shape, and general appearance; the great similarity between the yeast cells and bacteria of each in appearance, habits, mode of growth, form, and size; the fact that both of these yeasts cause alcoholic fermentation of milk; the fact that the drink formed by the American kephir closely resembles the description of kephir; the minor resemblance between the two, that of fermenting dextrose solutions, and that of its great capacity for resisting external influences, — we are justified in concluding the American milk-ferment to be a very near relative of the European kephir, if it be not indeed identical with it.

One point remains, viz. How can this yeast cause alcoholic fermentation of milk-sugar? This question, which did not present itself to Kern, De Bary has tried to explain in his 'Lectures on Bacteria.' Speaking of kephir, he says, "The changes in the milk which produce the drink here described are brought about by the combined activity of at least three ferment-organisms." There is the yeast cell, the Bacillus of the kephir-grain, and the Bacterium of lactic fermentation. He goes on to say that "the acidification is caused by the conversion of a portion of the milk-sugar into lactic acid by the bacterium of that acid. The alcoholic fermentation, that is, the formation of alcohol and of a large part at least of the carbonic acid, is indebted for its material to another portion of the milk-sugar, and for its existence to the fermenting power of the Sprouting Fungus (yeast). . . . But alcoholic fermentation is produced in milk-sugar as such neither by Saccharomycetes, with which we are acquainted, nor, as experiment has shown, by those of which we are speaking. To make this fermentation possible the sugar must first be inverted, split into fermentable kinds of sugar." De Bary continues: "According to Nägeli, the for-

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* Lectures on Bacteria, De Bary, translated by Garnsey and Balfour, p. 96.

mation of an enzyme which inverts milk-sugar is a general phenomenon in Bacteria, and Hueppe has shown that it is probable in the case of his Bacillus of lactic acid in particular." De Bary then concludes: "The inversion required in this case to enable the Saccharomycete to set up alcoholic fermentation is the work therefore of the Bacillus of lactic acid, or of the Bacterium of the Zoöglœa, or of both."

But De Bary has since revoked this explanation. A. Levy of Hagenau discovered that kephir may be made without any kephir grains "simply by shaking the milk with sufficient violence while it is turning sour. A trial convinced me," says De Bary, "of the correctness of this statement. The kephir obtained by shaking was not perceptibly different in taste or other qualities from the kephir of the grains, and the determination of alcohol, kindly made for me by Professor Schmiedeberg gave 1 per cent in some specimens of the former kind and 0.4 per cent in one of the latter; sour milk not shaken contained no trace of alcohol or only a doubtful one. Our former explanation, therefore, must be abandoned, and there is no other ready at present to take its place."

Beyerinck has also proposed a theory to account for alcoholic fermentation of milk. There are at present, he says, four yeasts which are known to cause such fermentation: (1) that of Duclaux,* (2) that of Adametz, called *Saccharomyces lactis*,† (3) that of the kephir called by Beyerinck *Saccharomyces kefyr*, and (4) *Saccharomyces Tyrocola*.‡ As a matter of fact there is one other which he overlooked, *Saccharomyces galacticola*, described by Pirotta,§ of which I intend to speak later. Beyerinck supposes that these yeasts secrete an enzyme which he names *lactase*, since it inverts lactose or milk-sugar, and which he declares to be in every way analogous with invertine. The inverted milk-sugar is next acted upon by the yeast, carbonic acid gas eliminated, and alcohol formed. Hence, if his supposition be true, *Saccharomyces kefyr* should ferment sweet milk by first producing its enzyme and then by acting upon the inverted product; but it is universally agreed by all who have written upon kephir that the lactic acid fermentation *must* precede the alcoholic, or else the latter will not take place. Beyerinck's theory therefore fails, in that it pays no heed to the Bacteria of lactic fermentation.

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* Ann. d. l'Inst. Pasteur, 1887, I. 573. See Ibid., 1889, III. 201.

† Centralblatt. f. Bakt. u. Parasit., V. 116.

‡ Ibid., VI. 44.

§ Pirotta et Rib. Studii sul Latte. Pavia, 1879.

I have experimented with our North American ferment and find the facts to be these: (1.) It causes alcoholic fermentation of milk-sugar or lactose, $C_{12}H_{22}O_{11}$. (2.) It causes fermentation of dextrose, $C_6H_{12}O_6$. (3.) It does not cause fermentation of saccharose or cane-sugar, which has the same empirical formula as lactose. In addition to these three facts it is also known, as Hueppe has shown, (1) that the Bacillus of lactic fermentation causes to some extent the inversion of milk-sugar; (2) that lactic acid, according to Hammarsten, by standing with milk-sugar inverts it to dextrose and galactose just as does any mineral acid; (3) that the Bacillus of lactic fermentation acts further on the galactose, $C_6H_{12}O_6$, converting it into two molecules of lactic acid, $C_3H_6O_3$.

From these data it seems evident that alcoholic fermentation of milk takes place in the following manner. The Bacillus acidi-lactis begins the process by forming some lactic acid, which in turn, assisted by the Bacillus itself, inverts the milk-sugar to galactose and dextrose. The galactose is further acted upon by Bacillus acidi-lactis and converted into lactic acid; the dextrose is acted upon by the yeast, and converted into alcohol and carbonic acid gas. In the kephir drink, therefore, we should find plenty of lactic acid, a little milk-sugar, not inverted, the amount depending upon the duration of fermentation, some alcohol, and carbonic acid gas, — precisely what is found.

One vital objection may, however, still be urged against this theory. If it be true, as I have said, that the Bacillus acidi-lactis to some extent, and the lactic acid to a greater extent, cause the inversion of milk-sugar, then should not ordinary beer yeast, *Saccharomyces cerevisiæ*, Meyen, cause alcoholic fermentation in sour milk, since the milk-sugar, according to the theory, must be here inverted to fermentable dextrose and to galactose? It should cause such fermentation; and if it does, the theory is confirmed. Upon experiment, I found that ordinary beer yeast when added to sour milk or to milk on the point of souring did cause fermentation, much carbonic acid gas being eliminated and some alcohol formed; sweet milk, however, did not ferment with beer yeast.

It will be observed that I have given no function to the Bacteria of the kephir granules. The very fact that they remain almost wholly in the Zoöglœa masses during fermentation, comparatively few going out into the milk, seems to indicate that they have little to do with this alcoholic fermentation; and this is made still more probable by the additional fact that, though absent in the fermentation of sour milk by beer yeast, still fermentation ensues.

To this theory De Bary has objected that kephir can be made simply by shaking milk which is on the point of souring, such kephir being called Pseudo- or Schüttelkephir. He refers to a paper by A. Levy,* of Hagenau, in which Levy claimed that ordinary sour milk shaken in a flask with eight or ten parts of cold boiled milk at about 10° R. gave carbonic acid gas, lactic acid, alcohol, and peptone. But Levy says, by shaking, the air is introduced, and the fermentation and peptonization are probably brought about by micro-organisms, which are very numerous in milk. Franz Kogelmann † has also published a method for obtaining kephir easily and cheaply. Take one volume of ordinary buttermilk, shake with two of fresh, and there is obtained a fluid "*identical* with kephir," containing carbonic dioxide, alcohol, lactic acid, casein, etc. Notwithstanding these claims, there is some doubt about the identity of Schüttelkephir and Kogelmann's kephir with the true sort, as Rudeck's ‡ table shows.

	Milk. One Litre.	Kogelmann's Kephir.	Pseudo Kephir.	True Kephir, 36 hours.
Casein	48.00	35.00	38.00	36.50
Butter	38.00	11.00	16.00	18.00
Lactose	41.00	9.00	13.00	18.00
Lactic acid	....	14.50	11.00	6.00
Alcohol	....	....	Trace	5.00
Albumen	1.80	....	"	1.50
Peptonized albumen . .	....	0.90	"	2.00
Lactosyntonid	....	0.40	....	0.80
Peptone	....	Trace	....	0.48
Salts and Water . . .	871.20	929.20	922.00	911.72
Totals	1000.00	1000.00	1000.00	1000.00

Despite this table, however, it is not improbable that alcoholic fermentation often does actually take place in Kogelmann's and Levy's methods, as the following paragraph may show.

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* Die wahre Natur des Kefirs. Deuts. Med. Ztg., 1886, p. 783.

† Ueber Milchwein (Kefir). Ibid. See also Pharm. Cent. Halle, XXVII. 42.

‡ Pharm. Ztg. Berl., XXXIII. 426.

Levy and Kogelmann were by no means the first to experiment on this subject. Blondlot,* as early as 1872, found that he could obtain alcoholic fermentation in milk simply by shaking it. Pirotta investigated this fermented fluid, and found a yeast, which he named *Saccharomyces galacticola*, identical with *Saccharomyces cerevisiæ* in appearance, size, spore formation, and in the fact that both ferment sour milk. It is not improbable, therefore, that this yeast may be nothing more nor less than *Saccharomyces cerevisiæ* itself, and that ordinary beer yeast is one of the micro-organisms which sprung up in Levy's kephir, of which he unfortunately omitted to make a microscopical examination. Hence De Bary's objection that sour milk, simply shaken, will give alcoholic fermentation, loses its significance.

Throughout Germany and Russia kephir has become a very celebrated drink, simply because a considerable portion of the albuminoids of the milk are peptonized. For persons of weak digestion, for children, and for dyspeptics generally, it is an excellent diet, since it relieves the stomach of much of its work. Hence the fame of kephir has spread far and wide, and a kephir factory has been started at Hamburg. The following table, taken from J. Biel's "Ueber die Eiweisstoffe des Kefirs," shows this peptonization very neatly.

In 100 parts of kephir were obtained: —

	Kephir fermented One Day.	Kephir fermented Two Days.	Kephir fermented Three Days.
Lactic acid	0.540	0.5625	0.6525
Lactose	3.750	3.2200	3.0940
Casein	3.340	2.8725	2.9975
Albumen	0.115	0.0300	0.0000
Acid albumen	0.095	0.1075	0.2500
Peptonized albumen . . .	0.190	0.2815	0.4085
Peptone	0.035	0.0460	0.0815

From the table it is evident that the casein and albumen decrease during fermentation, while the peptone, peptonized albumen, and acid albumen increase. This is shown still better by another table.

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* Comptes Rendus, LXXIV. 534.

In 100 parts of albuminoids were obtained: —

	Kephir fermented One Day.	Kephir fermented Two Days.	Kephir fermented Three Days.
Casein	88.47	86.07	80.20
Albumen	3.05	0.90	0.00
Acid albumen	2.52	3.22	6.69
Peptonized albumen . . .	5.03	8.43	10 93
Peptone	0.93	1.38	2 18

An analysis of the milk fermented by the American yeast shows the presence of peptone, in some quantity, whereas sour milk fermented by beer yeast gave only a trace, thus agreeing with Rudeck's analysis for Kogelmann's kephir. From these analyses there is but one inference, — the peptonizing power must lie, not in the *Bacillus acidilactis*, which is common to all these true and false kephirs, but in the yeast which Beyerinck has named *Saccharomyces kefyr*, and which exists in the United States.

In conclusion, I would return my thanks to Prof. W. G. Farlow and Prof. H. B. Hill, for advice given during the progress of my work.

X.

DAMPENING OF ELECTRICAL OSCILLATIONS ON IRON WIRES.

By John Trowbridge.

Presented May 27, 1891.

It has generally been assumed by those who have studied the subject of very rapid oscillations of electricity, such as occur in Leyden jar discharges, that the magnetic character of the conductor has very little influence upon the character of the discharge. Thus, in a note to an article on electrical waves, W. Feddersen states that electrical oscillations may suffer a slight weakening on iron; but this diminution is very slight: —

"Beim Eisen könnte in Folge der Magnetisirungen eine Abweichung hervortreten; in dess zeigt der Versuch, dass dieselbe keinenfalls bedeutend ist, übrigens in dem Sinne erfolgen müsste, als wenn die Elektricität beim Eisen ein grössere Hinderniss fände, wie bei den übrigen Metallen." *

In Dr. Lodge's treatise on Modern Views of Electricity (ed. 1889), we find the following: —

"But in the case of the discharge of a Leyden jar iron is of no advantage. The current oscillates so quickly that any iron introduced into its circuit, however subdivided into thin wires it may be, is protected from magnetism by inverse currents induced in its outer skin, and accordingly does not get magnetized; and so far from increasing the inductance of the discharge circuit, it positively diminishes it by the reaction effect of these induced currents; it acts, in fact, much as a mass of copper might be expected to do." (p. 365.)

Fleming writes as follows: —

"With respect to the apparent superiority of iron it would naturally be supposed that, since the magnetic permeability of iron bestows upon it greater inductance, it would form a less suitable conductor for discharging with great suddenness of electric energy. Owing to the fact that the current only penetrates just into the skin of the conductor,

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* Annalen der Physik und Chemie, No. 108, 1859, p. 499.

there is but little of the mass of the iron magnetized. Even if these instantaneous discharges are capable of magnetizing iron, . . . the electromotive impulses or sudden rushes of electricity do not magnetize the iron, and hence do not find in it any greater self-inductive opposition than they would find in a non-magnetic but otherwise similar conductor. Dr. Lodge's further researches seem to show that there is a real advantage in using iron for lightning conductors over copper, and that its greater specific resistance and higher fusing point enables an iron rod or tape to get rid safely of an amount of electric energy stored up in the dielective which would not be the case if it were copper." *

Fleming describes in full Dr. Lodge's experiments to prove the non-magnetizability of iron by sudden discharges: —

"In the experiments on alternative path, as described by Dr. Lodge, the main result is very briefly summed up by saying that, when a sudden discharge had to pass through a conductor, it was found that iron and copper acted about equally well, and indeed iron sometimes exhibited a little superiority, and that the thickness of the conductor and its ordinary conductivity mattered very little indeed. . . . In the case of enormously rapid oscillations the value of the impulsive impedance varies in simple proportion to the frequency of the oscillations, and depends on the form and size of the circuit, but not at all on its specific resistance, magnetic permeability, or diameter. . . . For discharges of a million per second and upwards, such as occur in jar discharges and perhaps in lightning, the impedance of all reasonably conducting circuits is the same, and independent of conductivity and permeability, and hardly affected by enormous changes in diameter." †

Turning now to the observations of Hertz, we find it stated that the material, the resistance, and the diameter of the wire of the micrometer circuit employed by him, have very little influence on the result. The rate of propagation of an electrical disturbance along a conductor depends mainly on its capacity and coefficient of self-induction, and only to a small extent on its resistance. Hertz concludes that, owing to the great rapidity of the alternations, the magnetism of the iron is unable to follow them, and therefore has no effect on the self-induction. When a portion of the micrometer circuit employed by Hertz was surrounded by an iron tube, or replaced by an iron wire, no perceptible effect was obtained, and thus the result was apparently

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* Fleming, Induction of Electric Currents, p. 398.

† Ibid., p. 411.

confirmed that the magnetism of the iron is unable to follow such rapid oscillations, and therefore exerts no appreciable effect. The velocity of propagation in a wire has a definite value independent of its dimensions and material. Even iron wires offer no exception to this, showing that the magnetic susceptibility of iron does not play any part in the case of such rapid motions.*

Although the impulsive impedance is apparently not affected by the magnetic character of the wire, experiments lead me to believe that discharges of the quick period of a Leyden jar are affected very appreciably by the magnetic nature of iron, steel, and nickel conductors. This effect is so great that it dampens the electrical oscillations, and makes it difficult to determine whether the time of oscillation is also affected by the permeability of the conductor.

The apparatus employed was similar to that described in the investigation of electrical oscillations with an air condenser.† Certain important modifications, however, were made. The plane mirror which was used in the former research was replaced by a concave mirror of ten feet focus and three and a half inches in radius. This mirror was mounted upon the end of the armature shaft of a one-half horse-power electric motor.

The discharging apparatus consisted of a sharp cutting tool, insulated, and mounted on the edge of the rotating disk bearing the mirror. It was metallically connected with a grooved ring of brass mounted upon the shaft and insulated from it by hard rubber. Around this was wound a copper wire, one end of which was connected with the discharging wire, and the other drawn taught by a rubber band. The electrical discharge was thrown on to the circuit by thrusting forward a lever which brought a solid hinged frame containing a strip of soft type-metal into contact with the rapidly revolving steel cutting tool. An electrical contact was thus insured by the tool cutting a groove in the strip of type-metal. In order to avoid a spark at the contact, the type-metal was thickly covered with a wax of peculiar composition. The only spark that occurred, therefore, was the one the oscillations

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* "Ersetzen wir den bisherigen Kupferdraht durch einen dickeren oder dünneren Kupferdraht oder durch einen Draht aus anderem Metall, so behalten die Knotenpunkte ihre Lager bei. Die Fortplanzungsgeschwindigkeit in allen solchen Drähten ist daher gleich, und wir sind berechtigt, von derselben als einer bestimmten Geschwindigkeit zu reden. Auch Eisendrähte machen keine Ausnahme von der allgemeinen Regel, die Magnetisirbarkeit des Eisens kommt also bei so schmalen Bewegungen nicht in Betracht." — Ann. der Physik und Chemie, No. 34, 1888, p 558.

† These Proceedings, Vol. XXV. p 109.

of which I desired to study. At each trial the type-metal was moved so as to expose a new cutting surface. The type-metal was insulated from the rest of the apparatus, but connected with the outer coating of the Leyden jar; first both terminals of the Holtz machine were thrown off, and immediately after the cutting tool, ploughing its way through the type-metal, placed the outer coating of the Leyden jar in circuit with one of the two parallel wires leading to the terminals of the spark. The other wire was permanently in connection with the inner coating of the jar.

Beside the short lead wires above described, the discharging circuit consisted of two parallel wires 30 cm. apart and 510 cm. long. These were the only portions of the apparatus changed during the experiment, and they were replaced by wires of different material and of different size. The other conditions — length of spark, lead wires, and the copper cross wire connecting the outer end of the long parallel wires — remained undisturbed throughout the experiment.

The Leyden jar was charged each time as nearly as possible to the same potential, judging by the number of turns given the Holtz machine. It is unfortunate that no more accurate means of measuring it were at hand, although the different negatives showed but slight variation. The capacity of the jar to alternations of this period was 5060 electrostatic units.

I describe the discharging portion of the apparatus minutely, for the success of an investigation of this nature depends upon the suppression of all sparks save that which one wishes to observe; and the method surely and completely accomplished this. The photograph of the spark could thus be made to fall very accurately on the sensitive plate. When one considers that the image of the spark was flying through the air on a circle of a radius of ten feet with a velocity of a mile a second, it will be seen that an extremely small deviation in the point of contact between the cutting tool and the type-metal would have thrown the image entirely off the sensitive plate. A singular phenomenon was noticed in this connection. When a comparatively low potential was used, such as that afforded by the air condenser used in our previous investigation, the cutting tool ploughed two or three millimeters along the surface of the type-metal before a spark passed at the point in the circuit where it was desired. With higher potentials this phenomenon was also observed, but the extent of cutting was diminished.

It is possible that that the insulating wax may have melted under the sudden blow of the cutting tool, and, flowing around it, prevented instant contact. This seems to us improbable, for a deep and clear-cut groove was made in the soft type-metal. Great attention was paid to the solid structure of this contact apparatus. It was entirely separate from the support of the revolving parts, and was perfectly steady.

The other end of the armature shaft was lengthened into a cylindrical chronograph, similar to that described in the article already cited, and its performance left nothing to be desired. A small Ruhmkorf coil, excited by two storage cells, and interrupted by a seconds pendulum, gave a record of the speed of the mirror. The stylus which drew the spiral turns on the barrel of the chronograph was drawn along the barrel by means of a small heavily loaded carriage, which, on being released at the moment the lever arm threw the type-metal in contact with the cutting tool, descended an inclined plane of adjustable height.

A small Töpler Holtz machine charged a large Leyden jar, and it was found to work admirably in all states of the weather. The apparatus which I have thus described was the result of the experience of the previous year, and worked for months without failure; and the taking of photographs of the oscillatory discharge by it became a mere matter of routine.

The following cases were tried: —

(1.) When the long parallel wires were of copper (diameter .087 cm.), the number of double oscillations visible on the negatives averaged quite uniformly 9 or 9.5.

(2.) When the wires were of German silver (diameter .061 cm.), three oscillations were visible.

(3.) But when an annealed iron wire (diameter .087 cm.) was substituted, only the first return oscillation was distinctly visible, with occasionally a trace of the first duplicate discharge.

(4.) On substituting fine copper wire (diameter .027 cm.), five complete oscillations were quite uniformly visible.

(5.) Fine German silver wire (.029 cm.), nickel wire (.019 cm.),* soft iron (.027 cm.), and piano steel wire (.027 cm.), gave but faintly the first return discharge after the pilot spark.

The pilot sparks were in all cases strong.

The single return discharge through the iron wire did not admit of measurement sufficiently accurate to furnish any basis for calculation of its self-induction. The time did not apparently differ, if at all, by

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* Obtained by the kindness of Joseph Wharton, Esq., of Philadelphia.

more than fourteen or fifteen per cent. Some general reasoning based upon the number of oscillations may be of interest. It must be acknowledged, however, that this reasoning is open to criticism, although it affords the most plausible explanation. The phenomenon itself is not a doubtful one.

The time of a double oscillation for the large-sized copper wire was .0000020 sec.; for the small copper wire, .0000021 sec. The others as far as could be determined did not differ much from these values, and for this purpose either is sufficiently accurate. Denote by R' the ohmic resistance of the parallel wires to alternating currents of this periodicity; by R. the resistance to steady currents.

$$p = \frac{2\pi}{t} = 3{,}000{,}000 \text{ (practically)}.$$

Taking the cases up in order:

(1.) Large copper wire,

$$R = 0.285 \times 10^9$$

and substituting in Lord Rayleigh's formula, $R' = \sqrt{\frac{1}{2} p l \mu R}$,

$$R' = 0.66 \times 10^9.$$

(2.) Large German silver wire,

$$R = 9.2 \times 10^9,$$

and substituting in the series

$$R' = R\left\{1 + \frac{1}{12}\frac{p^2 l^2 \mu^2}{R^2} - \frac{1}{180}\frac{p^4 l^4 \mu^4}{R^4} + \dots\right\},$$

$$R' = 9.2 \times 10^9.$$

(3.) Large iron wire,

$$R = 2.5 \times 10^9,$$

and if there is a true time lag, as often stated, such as to prevent action of the magnetic property of the iron, and if on this assumption we make $\mu = 1$,

$$R' = 2.78 \times 10^9.$$

(4.) Fine copper,

$$R = 3.3 \times 10^9,$$

$$R' = 3.5 \times 10^9.$$

(5.) Again, as before, call $\mu = 1$ in iron, nickel, and steel. The length of these circuits was 7.41 meters, the remainder of the 10.20 meters — 2.79 meters — being of copper wire of $R' = 0.94$.

The value of R' in the separate cases, including in each the resistance 0.94 of the copper portion, was as follows: —

Soft iron	15.0×10^9
Piano steel	20.7×10^9
Nickel	30.6×10^9
German silver	23.0×10^9

The ratio of the strengths of successive discharges during the oscillation is given by the function $\epsilon^{\frac{rT}{2L}}$, where r is the ohmic resistance, T the time of a double oscillation, and L the self-induction. The ratio of one discharge to the nth one after it is $\epsilon^{n\frac{rT}{2L}}$. If we assume — and it is a large assumption, but one which perhaps the result will in some measure justify — that the ratio of the strength of the first to the strength of the last visible discharge is more or less a constant, we may make use of the above data. Denote $\frac{T}{2L}$ by A, and call the unknown resistance of the short connecting lead wires and of the spark x. Then will $r = R' + x$, and n will be the number of complete oscillations visible.

Take cases (1) and (2), large copper and large German silver wires: —

$$\epsilon^{n_1(R'_1 + x)A} = \epsilon^{n_2(R'_2 + x)A}\ ;$$

$$n_1\ (R'_1 + x) = n_2\ (R'_2 + x)\ ;$$

$$9.5\ (0.66 + x) = 3\ (9.2 + x)\ ;$$

$$x = 3.4 \text{ ohms.}$$

Taking cases (1) and (4) similarly,

$$n_1\ (R'_1 + x) = n_4\ (R'_4 + x)\ ;$$

$$9.5\ (0.66 + x) = 5\ (3.5 + x)\ ;$$

$$x = 2.6 \text{ ohms.}$$

Experiments with other copper wires having R' equal to 3.4 and 1.27 gave 5 and 8 for the values of n respectively, or

$$x = 2.4 \text{ ohms.}$$

The resistance (R') of the lead wires forming part of x was 0.8 ohm, leaving as a possible value for the resistance of the spark about 2 ohms.

If, taking this value of x, we calculate the value of R' necessary to damp out the oscillation in one complete double discharge in the case of the large iron wire, we shall have

$$9.5\ (0.66 \times 3) = 1\ (R' + 3)\ ;$$

$$R' = 30 \text{ ohms.}$$

But neglecting the magnetic property of the iron, its calculated resistance to alternating currents of this periodicity was $R' = 2.78$ ohms. This is obviously inadequate, and would point to the conclusion that the oscillation is not, as sometimes stated, too rapid to admit of the magnetic action of the iron.

If we substitute this value $R' = 30$ in the equation

$$R' = \sqrt{\tfrac{1}{2} p l \mu R},$$

we have for the resulting value of the magnetic permeability $\mu = 230$. This lies between the limits $\mu = 103$ and $\mu = 1110$, found by taking the number of oscillations one and a half and one half respectively for the case of the iron wire.

It should be noticed that this estimate of μ necessitates assuming that T and L remain the same within broad limits. Measurements of the single oscillation on the negatives show that this is near enough the case. Part of the more rapid decay of the oscillation in the iron may be well ascribed to the dissipation of energy by hysteresis. While we cannot place much reliance upon an estimate of its value in such a case, — its percentage effect probably increasing rapidly with the decay of the spark, — it is not difficult to show that its influence may be very great.

There still remains the fact, not generally recognized, that, in Leyden jar discharges through iron wires, the magnetic property of the iron has time very materially to modify the character of the spark.

We give an example of the measurement of the half-oscillation which was the only one visible on the photograph of the discharge over iron wires, all the others having been dampened or extinguished by the iron, in comparison with the measurement of the similar half-oscillation on copper wires of the same diameter as the iron wires. The number of oscillations on the copper wires was eight.

The total duration of the discharge on iron wires was only three millionths of a second, while that on similar copper wire was three hundred-thousandths of a second. A steel wire gave the same results as the annealed iron wires.

Comparative Lengths of First Half-oscillation in Millimeters.

FINE IRON WIRE.	FINE COPPER WIRE.
.23	.19
.21	.20
.19	.20
.21	.19

Large Iron Wire.	Large Copper Wire.
.20	17
.20	18
.19	.20
.19	.18

I wish to express my deep obligations to my assistant, Mr. W. C. Sabine, for his valuable suggestions and for his skill in the mechanical details of this investigation.

Conclusions.

1. The magnetic permeability of iron wires exercises an important influence upon the decay of electrical oscillations of high frequency. This influence is so great that the oscillations may be reduced to a half-oscillation on a circuit of suitable self-induction and capacity for producing them.

2. It is probable that the time of oscillation on iron wires may be changed. Since we have been able to obtain only a half-oscillation on iron wires, we have not been able to state this law definitely.

3. Currents of high frequency, such as are produced in Leyden jar discharges, therefore magnetize the iron.

Jefferson Physical Laboratory,
Cambridge.

XI.

CONTRIBUTIONS TO AMERICAN BOTANY.

By Sereno Watson.

Presented April 8, 1891.

1. *Descriptions of some new North American Species, chiefly of the United States, with a Revision of the American Species of the Genus* Erythronium.

Arabis Macounii. Biennial, branched from the base, slender, pubescent below with mostly stellate spreading hairs, glabrous above or but sparingly puberulent, a foot high: leaves small and narrow, ½ inch long or less, the lower very rarely few-toothed, the cauline sagittate at base: flowers very small, pale rose-color, 2 lines long: pods very narrow, 1 to 1½ inches long and about ½ line broad, glabrous, slightly curved, mostly divaricate on very slender pedicels 2 to 4 lines long, acute, the stigma nearly sessile: seeds (immature) approximately 1-rowed, apparently wingless. — At Revelstoke, British Columbia; collected by Prof. John Macoun, May, 1890. Near *A. hirsuta*.

Erysimum arenicola. Caudex much branched and densely tufted, the branches slender; flowering stems about 6 inches high: leaves narrowly oblanceolate, sparingly toothed, acute or acutish, attenuate to a slender base, about an inch long, sparsely appressed-pubescent: pedicels slender, spreading and 2 or 3 lines long in fruit: calyx 4 lines long: pods ascending, slender, 1½ to 2 inches long and less than a line broad, compressed and thin-valved, usually attenuate above to a slender style tipped by the depressed lobed stigma: seeds narrowly oblong, a line long; the cotyledons very obliquely incumbent. — In volcanic sand on the Olympic Mountains, Washington, at 5,000 feet altitude; collected by Mr. C. V. Piper, September, 1890 (n. 916).

Silene Macounii. Stems very slender, from a slender branching rootstock, a foot high, minutely puberulent, glandular above: leaves linear-oblanceolate, 3 inches long or less: flowers few, on pedicels ½ to 1 inch long; calyx inflated, oblong-campanulate, 4 or 5 lines long, with short obtuse teeth; petals little exserted (6 lines long), with a broadly auricled glabrous claw and large thin quadrate and nearly entire appendages, the flabelliform bifid blade with a linear tooth on each side: capsule equalling the calyx, oblong-ovate, on a carpophore 1½ lines long. — Summit of the Rocky Mountains, British Columbia; collected by Prof. J. Macoun, August, 1890.

Mimulus (Eumimulus) filicaulis. A dwarf annual with very slender and thread-like lax stems, 1 to 4 inches high, simple or nearly so, sparsely glandular-pubescent: leaves thin and nerveless, entire, oblanceolate or oblong or the lowest obovate, obtuse, narrowed to a very short petiole: flowers on long pedicels, the narrowly oblong or turbinate calyx 3 lines long, acutely and unequally toothed; corolla funnelform with a nearly equally lobed limb, 7 to 9 lines long, bright rose-color in various shades, with more or less of purple and yellow in the throat and tube. — Collected by J. W. Congdon on Snow Creek, Mariposa County, California, in June, 1890. Near *M. Palmeri*, from which it differs in its much more slender and less branching habit, the leaves more narrowed at base, the calyx-teeth acuter, and the corolla different in shape and coloring.

Cladothrix cryptantha. Apparently annual, canescent throughout with a fine dense much branched pubescence, slender, repeatedly branched somewhat di- or trichotomously: leaves alternate, or subopposite at the forks, ovate to obovate, 4 to 6 lines long or less, on slender petioles: flowers in close clusters of 2 to 5, involucrate and more or less enclosed by two or more sessile floral leaves which are united below into a somewhat indurated cup; bracts and bractlets minute; sepals thin, ½ line long: utricle included, thin and hyaline, obtuse, the 2-lobed stigma nearly sessile. — Collected by Dr. C. C. Parry at Colton, California, in 1881 (n. 274), and by Mr. C. R. Orcutt in November, 1890 (n. 2186), at Canso Creek in San Diego County.

Eriogonum (Ganysma) minutiflorum Of the *E. pusillum* group, very slender, 6 inches high or less, diffusely branching, glabrous, excepting the small ovate rosulate leaves which are densely white-tomentose on both sides, becoming less tomentose above; bracts minute; peduncles filiform, divaricately spreading, 3 to 8 lines long; involucres very small (⅓ line long), broadly turbinate-campanulate, purplish: perianth yellow, minutely puberulent, very small. — Found by Mr. C. R. Orcutt in the desert region of San Diego County, California, April, 1890. Resembling *E. subreniforme*, but the leaves not reniform nor cordate, and the smaller flowers more pubescent.

Eriogonum deserticola. Apparently an annual of the same group (base and foliage unknown), tall, several times dichotomously branched, white-tomentose becoming mostly glabrous and yellowish green; bracts all small and deltoid; involucres shortly pedicellate or subsessile toward the end of the branches, erect or spreading, turbinate-campanulate, a line long: perianth villous, the elliptical segments yellow with greenish or reddish midveins, 1 to 1½ lines long. — In the southwestern part of the Colorado desert, San Diego County, California; C. R. Orcutt, November, 1890 (n. 2189).

ERYTHRONIUM, Linn. It is within the limits of the United States that this genus reaches its fullest development. On this continent it is found scarcely beyond our own boundaries, and in the Old World it shows a far narrower range of variation than here. Much unavoidable uncertainty has long existed respecting the species of western North America. Having taken advantage of such opportunities as presented themselves for studying these various forms, I now propose, though with some hesitation, the following revision of the genus. For material and for field-notes upon the difficult western species, thanks are due especially to Mr. Carl Purdy, G. R. Kleeberger, and Volney Rattan, of California, Mrs. P. G. Barrett, Thomas Howell, and W. C. Cusick, of Oregon, L. F. Henderson and W. N. Suksdorf, of Washington, and Prof. John Macoun of the Canadian Geological Survey.

The eastern and western species are conveniently separated, as will be seen, upon good distinctive characters. The Old World species, considered as a unit, is most nearly allied to the eastern group in its always solitary flowers, the want of a gibbous crest upon the petals, and the shape of the capsule, while in its mode of underground propagation it more resembles the western species.

The characters that must be relied upon for the distinction of species are rarely constant. The thinly coated corms produce new ones, either as in the eastern species at base within the old coats or at the extremity of long offshoots, or as in nearly all the western species along a rhizome, sometimes in near succession for several years, sometimes at intervals of an inch or less. The habit of spreading by offshoots, where it occurs at all, appears to depend much upon the season or locality, and is usually attended with a diminished production of flowers and seeds. The form of the leaves is only exceptionally of any value. In all the species the leaves in the cauline pair are unequal, one being as a rule narrower and more acuminate than the other. The mottling varies greatly in degree in the same species, or may even be wholly wanting, and like the minute dotting, which is generally present, it very often disappears in dried specimens. Only in *E. propullans* do the petioles form a closed sheath about the peduncle, and only in *E. Hartwegi* are they alternate instead of opposite.

The auricles or appendages at the base of the inner petals are uniform and constant, so far as known, in each species where they occur, though always greatly obscured in other than fresh flowers. Of the eastern species, *E. Americanum* is the only one with such special organs, having a rather thickened auricle upon each side of the petal, somewhat as in *E. dens-canis.* The western species, with the exception of *E. Howellii*, have the inner petals appendaged with a transverse crest of four more or less saccate gibbosities, the two inner the more prominent, the outer forming lateral auricles, so that the crests of the three petals when appressed to the ovary close completely over the basal cavity of the perianth. These crests differ in some degree in the different species, but usually not in such a way as to make a description of the differences easy; nor have they all been examined in the fresh flower.

The stamens show little that is specifically characteristic. They are in two unequal series, with more or less dilated filaments, the yellow, white, or occasionally purple anthers varying in length under different conditions, a moistened anther becoming very much longer than the same when dry. The relative lengths of the style and stamens vary with the age of the flower. The coherence or divergence of the stigmas appears to be in general a good sectional character. In all cases, however, the stigmas are at first coherent, and where separation occurs it may be more or less delayed after anthesis and more or less complete. Even in species with persistently coherent stigmas it is probable that separation occasionally occurs. The form of the capsule, while differing in the two groups, is essentially uniform in each. In the western species it varies much in length, in some species more acute than in others, in some proportionately wider. No marked differences have been observed in the seeds.

* Eastern species. Corm small (6 to 9 lines long), oblong-ovate, often propagating by lengthened offshoots, but also producing new corms more or less frequently at the base of the old: scapes low, 1-flowered: inner petals not crested: capsule obovate (mostly 5 to 9 lines long).

+ Offshoots produced from the base of the corm.

1. E. AMERICANUM, Ker. Leaves mottled: flowers yellow, often tinged without with purple and finely dotted within; segments 10 to 20 lines long, the inner auricled near the base: style scarcely lobed at the summit. — Bot. Mag. t. 1113; Bigelow, Med. Bot. t. 58; Barton, Fl. N. Amer. t. 33; Gray, Struct. and Syst. Bot., fig. 1247–1251;

Meehan, Nat. Flowers. 1st Ser., 1, t 17. *E. flavum*, Smith; Raf. Med. Fl. fig. 35. The "*E. Carolinianum*, Walt." of Poiret, Roemer & Schultes, etc., was based upon Walter's "*Anonymos, Erythronio affinis?*," which must have been *Uvularia perfoliata*. Damp open woodlands and banks; Nova Scotia to Ontario and Minnesota, and south to Florida and Arkansas.

2. E. ALBIDUM, Nutt. Leaves mottled: flowers white with more or less of a bluish or purplish tinge, yellow within near the base, not dotted, the segments strongly recurved, not at all auricled: stigmas short (1 to 1½ lines long), becoming recurved. — Similar localities: eastern New York to Ontario and Minnesota, and south to Pennsylvania, Virginia, Tennessee, and central Texas. The var. *coloratum*, Sterns (Torr. Bull. 15. 111), is the more deeply colored form.

3. E. MESOCHOREUM, Knerr. Resembling the last, but the leaves narrower (¼ to 1 inch wide) and not mottled; segments of the perianth not recurved; capsule larger (6 to 15 lines long). — Grassy prairies or wooded slopes, from western Iowa to central and eastern Kansas. First noted, as a variety of *E. albidum*, by Mr. R. Burgess (Bot. Gaz. 2. 115) and Mr. M. H. Panton (same. 2. 123); perhaps well separated from that species by Prof. E. B. Knerr (Midland College Monthly, 2. 5).

+– +– Offshoots produced from the sheathed portion of the scape.

4. E. PROPULLANS, Gray. Leaves small (2 to 4 inches long) above the close sheath, from within the base of which the offshoot springs, slightly mottled: flowers rose-color with yellow base, small (½ inch long), the inner segments not grooved nor auricled: stigmas united; capsule unknown. — Am. Nat. 5. 228, fig. 74. Southern Ontario (*fide* Macoun); southern Minnesota.

* * Western species. Corms usually elongated, rarely if at all propagating by offshoots (except in n. 6), the new corms borne upon a short rhizome: scapes often tall, 1-several-flowered: inner petals auricled and transversely crested at base (except in n. 11) with four prominent gibbosities: capsule oblong, attenuate below.

+– Stigmas at length distinct and recurved.

++ Leaves not mottled (or rarely?): flowers bright yellow.

5. E. GRANDIFLORUM, Pursh. Scape 1- (rarely 2–3-) flowered, becoming 1 or 2 feet high: perianth strongly recurved, 1½ to 2 inches long: capsule 1 to 2 inches long, rounded or slightly retuse at the summit. — Lindl. Bot. Reg. t. 1786. *E. grandiflorum*, var. *minus*, Hook., Morren, etc. Mountains of northern Idaho, Washington, and British Columbia near the boundary.

Var. PARVIFLORUM. Scape usually low; flowers smaller, the segments 12 to 15 lines long. — *E. Nuttallianum*, Regel, Gartenfl. t. 695, not R. & S.; *E. grandiflorum*, Murray, Gard. Chron. 1871, fig. 173. In the mountains from Colorado and northern Utah to British America, in the Blue Mountains of Oregon, and in the Cascade Mountains of Washington and British Columbia; the more common form.

The var. *Murrayi* of Morren (Belg. Hort. 26. 105, t. 6) is a doubtful cultivated form similar to this, but said to have mottled leaves. In a single specimen collected by Mr. Henderson above the timber-line on the Olympic Mountains, Washington, the leaves are evidently mottled.

++ ++ Leaves more or less mottled. Pacific Coast species.

= Corms producing slender offshoots from the base.

6. E. HARTWEGI, Watson. Corms small (6 to 8 lines long): leaves (rarely 3) often alternate: flowers 1 to 3, pale yellow with an orange base, the segments 1 to 2 inches long by 3 to 6 lines broad or more, spreading or scarcely recurved: capsule unknown. — Proc. Am. Acad. 14. 271. In the Sierra Nevada, California, from Mariposa to Plumas Counties. This species, or a similar one, is also reported from near Healdsburg, Sonoma County (*R. H. Thompson*).

= = Corms (1 to 2 inches long) produced in succession upon a usually short rhizome.

7. E. REVOLUTUM, Smith. Leaves attenuate to a usually narrow petiole: scape often over a foot high, 1–2-flowered: perianth "white" to pale yellow, yellow at base, the segments narrowly lanceolate (3 or 4 lines broad): capsule abruptly acutish at the apex, 12 to 15 lines long. — Rees' Cyc. *E. grandiflorum*, var. *Smithii*, Hook. *E. grandiflorum*, var. *revolutum*, Baker. Vancouver Island to the lower Columbia valley. Described by Smith as having purplish flowers, and an original specimen in Herb. Kew bears the note "fl. rubr. purp." by Sir W. J. Hooker, but it is rarely that the petals assume a pinkish tinge in drying, and the ground for the statement is unknown. No purple-flowered species is now found on Vancouver's Island, where Menzies's specimens were collected.

Var. BOLANDERI. Usually low, 1–3- (rarely 4-) flowered; perianth white with yellowish centre, becoming rose-purple; appendages very prominent. — In the redwoods of Colusa, Mendocino, and Trinity Counties, California.

8. E. GIGANTEUM, Lindl. Leaves narrowed to a usually short and broadly margined petiole: scape often tall, 1–6-flowered or more: perianth cream-color (often described as white) with a light yellow or

orange base and sometimes a transverse darker or brownish band, the segments more broadly lanceolate (1 to 1½ inches long by 4 to 7 lines broad): capsule oblong-obovate (7 to 9 lines long), very obtuse or retuse at the summit. — Hook. Bot. Mag. t. 5714 (*E. grandiflorum*, Fl. de Serres, t. 2117). *E. grandiflorum*, var. *albiflorum*, Hook. *E. giganteum*, var. *albiflorum*, Gard. Chron. 1888¹, fig. 74. From the lower Columbia valley southward to Mendocino and Sonoma Counties, California: March to June.

9. E. MONTANUM. Like the last, but the leaves (not mottled?) more or less abruptly contracted and rounded at base; scape 1–2-flowered; perianth white with an orange base, often drying pinkish. — On the high mountains of Oregon and Washington (Mt. Hood, Mt. Adams, etc.; *Mrs. P. G. Barrett, Howell*, and *Suksdorf*); in flower from July to September.

+ + Style short-clavate, undivided; scape a foot high or less; leaves mottled; corms as in the last group.

++ Inner petals appendaged.

10. E. CITRINUM, Watson. Corms unknown: scape 3-flowered: segments of the perianth broadly lanceolate, an inch long, strongly recurved, light yellow with an orange base, the tips becoming pinkish; crest rather thin: capsule unknown. — Proc. Am. Acad. 22. 480. Deer Creek Mountains, southern Oregon (*T. Howell*).

11. E. HENDERSONI, Watson. Scape 1–3-flowered: perianth 1 to 1½ inches long, strongly revolute, pale purple with a very dark purple and yellowish base, the lobes of the crest subglobose-inflated: capsule an inch long, very obtuse. — Proc. Am. Acad. 22. 479; Gard. Chron. 1888¹, fig. 86; Garden and Forest, 1, fig. 50; Bot. Mag. t. 7017. In the mountains of southern Oregon.

12. E. PURPURASCENS, Watson. Corm 1 to 2 inches long: leaves undulate: scape 1–8-flowered: perianth 9 to 12 lines long, spreading, light yellow tinged with purple, deep orange at base: capsule obtuse or retuse, 1 to 1¼ inches long. — Proc. Am. Acad. 12. 277. In the Sierra Nevada, from Placer to Plumas Counties, California. Inflorescence more crowded than in any other species.

++ ++ Inner petals not appendaged.

13. E. HOWELLII, Watson. Scape 1–3-flowered, perianth recurved, pale yellow with deep orange base, becoming pinkish: capsule unknown. — Proc. Am. Acad. 22. 480. Josephine County, southern Oregon (*T. Howell*).

ZOSTERA OREGANA. Stem slender: leaves 1½ to 2 lines broad, rather faintly 3-nerved: spathes 2 or 3 inches long, very obtuse, with a short scarious crest but without a foliar appendage at the summit; spadix short-acuminate: utricle with a long straight beak; seed (immature) narrowly oblong, with 16 longitudinal striæ. — Collected by Elihu Hall in 1871, probably near the mouth of the Columbia River, Oregon; in Herb. Gray, without number, and not mentioned in the published list of his distributed Oregon collection. Readily distinguished by the unappendaged spathe. The spadix examined was about 15-fruited; the anthers had all fallen.

ZOSTERA PACIFICA. Stem stout; cauline leaves 4 to 6 lines broad, 5–9-nerved, those on the branches 2 lines broad and 3-nerved: spathe nearly 3 inches long, with a long foliar appendage; spadix acutish, many-flowered: utricle with a long straight beak; seed broadly elliptical, compressed, 1½ lines long, not evidently striate but appearing under the microscope very finely transversely striolate. — About Puget Sound (*Rev. R. D. Nevius*); Monterey (*Dr. C. L. Anderson*); Santa Barbara (*Mrs. R. F. Bingham*). A specimen received from Mr. Nevius is eight feet long, with some of the leaves four feet in length. The anthers are mostly arranged in vertical pairs, alternating with solitary ovaries. The seed is remarkably distinct from that of *Z. marina*, which is shorter, oblong, terete, and conspicuously 20-striate. The species has been described by Mr. Morong (Torr. Bull. 13, 160) as *Z. marina*, var. (?) *latifolia*.

2. *Descriptions of new Mexican Species, collected chiefly by Mr. C. G. Pringle in* 1889 *and* 1890.

RANUNCULUS VAGANS. Near *R. hydrocharoides* and *R. stolonifer*, low, spreading by elongated stolons, glabrous: leaves narrowly lanceolate or the lowermost ovate-lanceolate, entire or with a few often slender teeth toward the apex: petals 8 to 10, oblong-obovate, about 2½ lines long and nearly twice the length of the sepals, with a prominent gland above the narrow claw: carpels smooth, in a dense globose head 2½ lines in diameter. — Found in shallow ponds near Flor de Maria in the State of Mexico, August, 1890 (n. 3177).

NASTURTIUM BRACTEATUM. Annual, erect, unbranched, glabrous or slightly and finely pubescent (6 inches high or less): leaves sessile, auricled at base, narrowly oblong, pinnately toothed, 6 to 9 lines long: raceme many-flowered and becoming elongated; fruiting pedicels divaricately spreading, 3 lines long, the lower solitary in the axils of the upper leaves: flowers apparently white, a line long: pod elliptical, 1½ to 2 lines long, beaked with a short style; stigma small. — *N. palustre*, Benth. Pl. Hartw. 9. Described from a few small but fruiting specimens in Herb. Gray, collected by Hartweg (n. 39) at Aguas Calientes in the Mexican State of the same name. The lower axillary pedicels are an unusual character.

SISYMBRIUM MULTIRACEMOSUM. Finely stellate-pubescent throughout, the lax and slender stems procumbent, branching, 2 feet long or more: leaves narrowly lanceolate, attenuate to both ends, not auricled at base, sinuately serrulate or sometimes serrate, 1 to 2 inches long: racemes in most of the axils, on very short leafy peduncles or nearly sessile, 1 to 3 inches long in fruit: flowers very small, white: pods divaricately spreading on pedicels about a line long, pubescent, narrow and subcylindrical, about 3 lines long, beaked by a short slender style: seeds in one row, 8 to 10 in each cell. — At Las Canoas, San Luis Potosi; October, 1890 (n. 3522). A species of strongly marked habit.

POLYGALA SUBALATA. Annual, the several stems erect from an ascending base, branching above, narrowly wing-angled, leafy, glabrous or slightly puberulent, 6 inches high or less: leaves mostly verticillate, oblanceolate, very acute, 4 to 6 lines long, scabrous on the margin, the lowermost small, obovate to spatulate and obtusish, the upper becoming linear; spikes sessile, dense, acuminate, becoming elongated and looser: flowers small, very shortly pedicellate; petals white with a broad green or purplish midvein: capsule very broadly elliptical, equalling the petals (a line long): seeds oblong, sparsely covered with a very fine appressed silky pubescence, the linear appendages of the hilum as long as the seed. — In low grounds at Flor de Maria, State of Mexico, September, 1890 (n. 3240). Resembling *P. alba*, especially its var. *suspecta*, from which it is most positively distinguished by the much less pubescent seed nearly equally broad at both ends.

TALINUM COAHUILENSE. Stems very short and leafy, from a slender branching rootstock or rhizome bearing oblong or ovate tubers: leaves rhombic-obovate, cuneate at base and nearly sessile, inflated-margined, ½ inch long or less: flowers solitary on short pedicels (½ inch long); sepals round-ovate, acute, strongly concave, 2 to 2½ lines long; petals round-obovate, 3 lines long: stamens numerous with very slender filaments and short anthers: capsule ovate. — On limestone hills at Carneros Pass, Coahuila: May, 1890 (n. 3606). Much resembling *T. brevifolium* and *T. brevicaule*, especially the latter, differing in the tuberous roots and broader leaves and sepals.

SIDA ALAMOSANA. Perennial (?), herbaceous, erect, slender and branching, finely glandular-pubescent: stipules filiform, 2 to 4 lines long; leaves on slender petioles, ovate to lanceolate, acuminate, more or less cordate at base, rather acutely serrate, 2½ inches long or less, somewhat hairy especially on the nerves (not glandular-pubescent), the hairs simple or forked: peduncles axillary, slender, mostly an inch long or more: corolla "orange" (apparently white), 3 lines long, exceeding the acuminate-toothed calyx: carpels 5, little over a line long, ovate, glabrous except the summit, thin-walled, terminating in a contracted truncate dehiscent cavity above the seed. — Collected at Alamos, Sonora, by Dr. Edward Palmer (n. 683) in September, 1890. Closely resembling *S. ulmifolia* in habit, but more glandular-pubescent, with longer filiform stipules, more acutely serrate leaves, and especially distinguished by the unusual character of the carpels.

AYENIA BERLANDIERI, Watson, Proc. Am. Acad. 21. 419, in part. Mr. Pringle has collected flowering specimens which accord in foliage with the original specimens of Berlandier, but with different flowers from those of the plants of Dr. Palmer's Chihuahuan collection upon which my description was largely based. It becomes necessary to separate the two forms and to redescribe this species. — Plant 3 to 6 feet high, the herbaceous branches more or less strongly angled and sulcate: leaves ovate to ovate-lanceolate, acute, rounded or slightly cordate at base, densely pubescent beneath with a soft stellate tomentum, greener above, serrulate, 2 to 4 inches long: peduncles 1–2-flowered, fascicled in the axils or in a naked terminal inflorescence: calyx and petals dark purple, the former 2½ lines long, the blade of the petal parted into two broad quadrate and truncate lobes: anthers 3-celled: ovary and capsule rather long-muricate. — Berlandier; Pringle (n. 3309), in low lands at Las Palmas, San Luis Potosi.

AYENIA JALISCANA. Differing from *A. Berlandieri* in its more terete branches and thinner, less pubescent, and more coarsely toothed leaves; flowers smaller and paler, the sepals 1½ lines long, and the lobes of the petals oblong and acutish; anthers 2-celled and capsule more shortly muricate. — Southwestern Chihuahua, Dr. E. Palmer (n. 19 and 83), and apparently also at Guaymas (n. 243 of his 1887 collection).

BUNCHOSIA PRINGLEI. A shrub or small tree (12 to 20 feet high); branchlets and inflorescence appressed-hairy: leaves thin, oblong, obtusely short-acuminate, acutish at base, eglandular, glabrous above, sparsely hairy beneath, 3 or 4 inches long by 1 or 2 broad, on petioles 3 lines long: racemes mostly solitary in the axils and simple, shorter than the leaves; pedicels glanduliferous, stout and 2 or 3 lines long in fruit: ovary pubescent, globose, beaked by the subpersistent style; fruit 2–3-lobed, the seeds 4 lines in diameter. — In Tamasopo Cañon, San Luis Potosi; July, 1890 (n. 3540). Near *B. lanceolata* of Turczaninow.

SARGENTIA (?) PRINGLEI. A shrub, 10 to 15 feet high: leaves coriaceous, pinnately 1-foliolate or sometimes palmately 3-foliolate, the lower surface (with the petioles and branchlets) pubescent with very short spreading hairs, glabrate above: leaflets oblong-oblanceolate, acutish or obtuse, cuneate at base, entire, puncticulate, 1 to 2½ inches long: sterile flowers small, in a very short terminal few-flowered panicle, with very short triangular sepals and 4 (or 5) narrow oblanceolate valvate petals, concave and spreading: disk inconspicuous or none, the stout filaments (usually 4) inserted at the base of the small abortive ovary: anther-cells distinct to above the middle, acute at base, rounded above: fruit on short stout pedicels solitary at the ends of short branchlets, depressed-globose (6 to 9 lines broad), mostly 2–3-celled and 2–3-seeded, the oblong-obovate seeds 6 lines long. — The fruit is essentially that of *S. Greggii*, though less lobed, but the flowers differ so widely in being usually tetramerous, with valvate petals, no disk, and dissimilar anthers, that the correctness of the reference to *Sargentia* is very doubtful. The fertile flowers are as yet, however, unknown. In *S. Greggii* the anthers are cordate with an acute apex. Found in the mountains of San Luis Potosi at San José Pass, in June, 1890, in fruit, and in July in flower (n. 3220). It appears to have been also collected by Berlandier in 1828 at Monterey, without flowers or fruit, the specimen in the Gray Herbarium without number, under the name of *Choisya ternata*.

XANTHOXYLUM PRINGLEI. A tree, becoming 40 feet high, glabrous: leaflets 3 to 5 pairs, lanceolate, acuminate, rounded at base, entire, coriaceous, epunctate or with a few large glandular dots near the apex, 1½ to 2½ inches long on petiolules 1 to 2 lines long: flowers diœcious, very numerous in large terminal corymbs; pistillate flowers with a very short 3-lobed calyx and three elliptical petals: carpels solitary; fruit globose, tuberculate, 1½ lines in diameter. — In Tamasopo Cañon, San Luis Potosi, in June, in flower; October, in fruit (n. 3102).

NEOPRINGLEA. As the genus *Llavea* of Liebmann is long antedated by the *Llavea* of Lagasca, a genus of ferns that is generally considered as well founded, it is necessary to substitute another name for that of Liebmann. I take pleasure in dedicating the genus to one most worthy, whose botanical collections in Mexico have been unexcelled in character and who has added very greatly to our knowledge of the Mexican flora.* The genus has hitherto been placed provisionally in the *Celastraceæ*. Its affinities are rather with *Alvaradoa* in the *Sapindaceæ*.

NEOPRINGLEA INTEGRIFOLIA. (*Llavea integrifolia*, Hemsl.) Complete specimens of this hitherto imperfectly known diœcious shrub have been collected by Mr. Pringle on San José Pass, San Luis Potosi: in flower, July (n. 3137), and in fruit, October (n. 3248). The staminate flowers are in short crowded axillary racemes, tetramerous, the four greenish petals orbicular, pubescent, not exceeding the sepals: stamens 12, in threes opposite to the petals, in the sinuses and intervals between the pubescent lobes of the disk; pistillate flowers without petals or disk, the 3-winged ovary 3-celled at base, with solitary anatropous ovules on the axis: capsule 1-celled, 1-seeded; seed compressed-obovate, the embryo straight in rather thin albumen, with flat cotyledons and rather slender inferior radicle.

DESMODIUM SUBSPICATUM. Stems erect from a narrow fusiform root, somewhat woody at base, glabrous or slightly puberulent, 18 inches high: leaves nearly sessile, the single leaflet linear-lanceolate, obtusish at base, acuminate and very acute, 1 to 3½ inches long, glabrous or nearly so: racemes pubescent, terminal, simple and spike-like, the small greenish flowers solitary or in pairs, on pedicels a line long or less, the lanceolate bract about equalling the calyx: legumes erect, pubescent, 9 lines long or less, 3–5-jointed, nearly equally indented on both sutures and the joints elliptical. — On grassy hillsides at Las Canoas, San Luis Potosi; July, 1890 (n. 3211). Near *D. angustifolium*, DC., as that species is described.

DESMODIUM AMANS. Tall, erect, the stem, petioles and inflorescence clothed with short hooked hairs: stipules attenuate from a broad base, villous; petioles about ½ inch long; leaflets rather thick and reticulately veined, narrowly oblong, acute, rounded at base, glabrous above, villous beneath, 1½ to 2 inches long by 6 lines broad; stipels subulate, attenuate: racemes in a naked terminal panicle; bracts ovate, acuminate, 3 lines long; pedicels becoming 3 or 4 lines long: calyx-teeth exceeding the tube, unequal, the lower longer and narrower; petals purple, 3 lines long: legume 5–7-jointed, with the two sutures nearly equally sinuate, the suborbicular joints 1½ lines

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* The *Pringleophytum* dedicated to Mr. Pringle by Dr. Gray is identical with *Berginia*, Harvey, as was first suggested by Mr. Brandegee.

broad, densely uncinulate-hispid. — On hillsides at Las Canoas, San Luis Potosi; October, 1890 (n. 3291).

COLOGANIA JALISCANA. This name is to be substituted for *C. Pringlei* upon page 147 of the last volume of the Proceedings, on account of a previous species so named in Mr. Pringle's collection of 1887.

BEGONIA (WEILBACHIA) PRINGLEI. Rhizome slender, covered with brown ovate acuminate glabrous stipules: petioles tomentose, 2 to 4 inches long; leaves obliquely rhombic-ovate, acute, cordate at base, coarsely and subsinuately toothed, sparsely pubescent above, somewhat tomentose and densely papillose beneath, 2 or 3 inches long: peduncle 4 to 8 inches high, red, slightly pubescent, 4–6-flowered at the summit: flowers apetalous, the two sepals round-reniform or orbicular, 4 to 6 lines broad: fruit with two broad truncate-rounded wings, the third smaller. — On cold ledges in Tamasopo Cañon, San Luis Obispo; October, 1890 (n. 3514).

ERYNGIUM MEXICANUM. A span high, spreading, twice branched: basal leaves with a nodose petiole sheathing at base, the blade linear or linear-lanceolate, sparsely serrate, usually with a pair of similar but shorter lobes at base; cauline leaves nearly sessile, similar: heads pedunculate, ovate or oblong-ovate, 4 to 6 lines long, terminated by one or sometimes two or three slender foliaceous appendages, entire or occasionally cleft above, and subtended by about ten longer linear acute bracts, whitish above and usually with a slender tooth on each side; bractlets none or minute: fruit covered with numerous white scales, the calyx-lobes dark blue. — In wet meadows at Del Rio, State of Mexico; August, 1890 (n. 3229).

ARRACACIA MARIANA. Stems decumbent from a branching caudex, slender, simple or sparsely branched, a foot long, glabrous: leaves near the base, thin, pinnate, the leaflets 4 or 5 pairs, an inch long or often much less, acute, sharply serrate, the lower usually with a pair of linear lobes at base: umbels on long terminal peduncles: bracts of the involucre and involucels narrowly linear: rays (6 to 10) in fruit 4 or 5 lines long: flowers yellow: fruit nearly sessile, ovate, acutish, 3 or 4 lines long, strongly and obtusely ribbed; ventral sinus of the seed completely closed. — On hillsides at Flor de Maria, State of Mexico; July, 1890 (n. 3480).

ARRACACIA MULTIFIDA. Tall and stout, glabrous: leaves ample (a foot long or more), sessile upon a short sheathing base, ternate and several times pinnate, the ultimate segments very narrowly linear, entire, acute, an inch long or usually less: umbels on stout peduncles, without involucre or involucels; rays numerous, 1 to 1¾ inches long in fruit; pedicels 2 or 3 lines long: fruit 3 or 4 lines long, oblong, the carpels narrowed at each end and beaked by the stout erect stylophore and style, acutely angled by the thin prominent ribs; vittæ quite variable, 1 to 3 in the broad intervals and usually 2 on the narrow commissure; the deep sulcus very narrow. — On hills at Rio Hondo, State of Mexico; August, 1890 (n. 3620).

CHOMELIA PRINGLEI. A small tree (15 feet high); branchlets pubescent with short spreading hairs: leaves oblong-ovate, rounded at base, short-acuminate, finely pubescent beneath, slightly scabrous above, 1½ to 3 inches long, on petioles 1 or 2 lines long: peduncles slender, 6 to 12 lines long; flowers few, sessile or nearly so, subcapitate or in a very small loose cyme; calyx pubescent, equally toothed, scarcely a line long; corolla reddish, 3 or 4 lines long, rather broadly tubular and but slightly dilated above, the lobes appressed-pubescent, a line long: fruit compressed-oblong, sparsely pubescent, 3 lines long. — In Tamasopo Cañon, San Luis Potosi; August, 1890 (n. 3209).

CRUSEA MEGALOCARPA. (*Spermacoce megalocarpa*, Gray, Proc. Am. Acad. 21. 381.) Collected by Mr. Pringle in the barranca near Guadalajara; September, 1889 (n. 2968). This species was referred by Dr. Gray to the section *Borreria* of *Spermacoce*, but the chartaceous cocci separate from a persistent septum which is cleft nearly to the middle and crowned by the persistent linear-lobed calyx-limb. It therefore accords perfectly with *Crusea* as that genus was characterized in De Candolle's Prodromus and by Bentham & Hooker in the Genera Plantarum. The "calycis limbi lobi persistentes" of the latter is criticised by Dr. Gray, and rightly if it were to be understood as meaning that the calyx-limb is persistent upon the cocci. It always separates from the cocci, and may either remain persistent upon the persistent axis, as is the statement of De Candolle, or break away from this also, as in *C. subulata* and some other species.

EUPATORIUM MADRENSE. Branches woody, slender and lax, the branchlets finely pubescent, leafy: leaves opposite, small (an inch long), very shortly pedicellate, ovate-lanceolate, acute, rounded or subcordate at base, 3-nerved, serrate except toward the apex, roughish above, tomentose beneath: heads few (3 to 6), terminal and axillary on short peduncles, many-flowered, narrow below, 4 lines high; involucre 3 lines long, shorter than the disk, its unequal scales in several series, nerved, subtomentose, acute, the outermost narrowly ovate, the innermost linear: achenes slightly hispid toward the base on the acute angles; pappus in a single series, slightly scabrous. — In the Sierra Madre near Monterey; June, 1888 (n. 2201).

EUPATORIUM (?) CHAPALENSE. Woody, the branches terete, glabrous: leaves opposite, ovate-lanceolate, acute, rounded at base but decurrent upon the slender petiole, 3–5-nerved above the base, serrate, puberulent above on the veins and villous-tomentose on the nerves beneath, 1½ to 2½ inches long, the petioles about an inch long: heads on slender bracteate puberulent peduncles in a dense terminal corymb, 20-flowered or more, narrow at base; involucral scales mostly nearly equal, 4 lines long, thin, linear, acute, pubescent; receptacle depressed-conical, smooth and naked: achenes (immature) apparently obtusely pentagonal, papillose; pappus-bristles in more than one row, distinctly barbellate, unequal, the outer very short. — In the mountains near Lake Chapala; December, 1889 (n. 2974). Near *E. multiserratum*, Schultz Bip., in habit and involucre, but the pluriseriate unequal pappus is abnormal. The unequal pappus suggests *Piptothrix*, but the setæ are much more numerous and not caducous, while the heads, flowers, and pappus are twice longer than in either of the species of that genus.

OLIGONEMA, a new genus of the homochromous *Asteroideæ*. Heads many-flowered, radiate and heterogamous, the ray- and disk-flowers all fertile. Involucre broadly campanulate, of many nearly equal herbaceous scales in several series, the inner series becoming somewhat coriaceous with herbaceous tips. Receptacle nearly flat, naked. Ligules linear, yellow, slightly 3-toothed; disk-corollas tubular, the throat scarcely dilated and about equalling the oblong acute lobes. Anthers obtuse at base. Style-branches tipped with attenuate conical appendages. Achenes of the ray compressed-triangular, those of the disk obcompressed, elliptical, glabrous, rather thin-margined, truncate, the thickened margin of the summit bearing 1 to 4 very delicate lax scabrellate deciduous hairs. — A stout annual aquatic or marsh herb, with alternate linear entire leaves, the submerged pinnately parted; heads rather large, terminal on the branches. A genus most nearly related to *Grindelia*, strongly marked by its habit and the characters of the achenes and pappus.

O. HETEROPHYLLA. Mostly glabrous, somewhat glandular-pubescent above, the stem 2 or 3 feet high, fistulous, sending out delicate rootlets from the submerged nodes: leaves sessile, clasping, acuminate, 2 or 3 inches long, the submerged pinnate with narrowly linear entire or toothed segments: heads half an inch broad, the orange ligules 6 to 8 lines long; involucral scales lanceolate, acuminate: achenes about 1½ lines long, somewhat longer than the delicate pappus. — In shallow water at Del Rio, State of Mexico; August, 1890 (n. 3236).

Achætogeron linearifolius. Biennial or perennial (?), branching from the base, the stems ascending or decumbent, a foot high or less, somewhat strigose-pubescent: leaves numerous, dark green, narrowly linear, entire or rarely with one or two narrow lateral lobes, mostly 1 to 1½ inches long, acute, narrowed to the base: heads hemispherical (4 or 5 lines in diameter), with hemispherical receptacle and linear acuminate involucral bracts: rays very numerous in several rows: achenes (immature) compressed (?), sparsely hispidulous; pappus coroniform, dentate and laciniately denticulate, nearly as long as the proper tube of the corolla. — Bluffs and plains near Flor de Maria, State of Mexico; Sept., 1890 (n. 3242). The distinctions between the genera *Aphanostephus* and *Achætogeron* are very vaguely defined, the latter genus appearing to rest upon the compressed Erigeron-like achenes.

Psilactis tenuis. Erect, slender (2 feet high), branching above, the slender spreading branches simple or few-flowered, rough-hispid with spreading hairs: cauline leaves oblong-oblanceolate, acute, narrowed to a short winged petiole, sharply serrate, 1 to 1½ inches long, those on the branches gradually smaller and narrower: heads solitary and terminal, small (2 lines high); involucral scales thin and scarcely herbaceous, narrowly linear, acuminate: ligules purplish, 3 lines long: achenes sparsely pubescent; pappus of disk-achenes of numerous (about 30) barbellate setæ. — In the Sierra Madre near Monterey; June, 1888 (n. 2238).

Aster Carnerosanus. Stems a foot high or less, from slender rootstocks, slender, purplish, pubescent: leaves oblanceolate, 1½ inches long or less, mostly entire, glabrous or nearly so, shortly ciliate, the bracteal oblong, 2 or 3 lines long: heads middle-sized (5 lines high), solitary on the short branches, the numerous foliaceous-tipped scales somewhat spreading, oblanceolate, acute or the innermost subacuminate: rays pale purple. — At Carneros Pass in the mountains of Coahuila; Sept., 1889 (n. 2859). Rather closely resembling *A. surculosus* of the Alleghanies, but with smaller heads.

Melampodium glabrum. Nearly glabrous (slightly scabrous above, especially on the peduncles), decumbent, branching: leaves oblong- to linear-lanceolate, scarcely narrowed to the broad clasping base, acutish, sparingly toothed, 1¼ inches long or less: heads small (2 to 2½ lines high), on slender peduncles, the 5 or 6 ovate scales obtuse or acutish: ligules oblong, shorter than the scales, yellow:

achenes triangular-obovate, over a line long, transversely rugose. — Valley near Irapuata, Guanajuato; Sept., 1889 (n. 2821). Near *M. montanum.*

MELAMPODIUM (UNXIA) BIBRACTEATUM. Annual, glabrous, a foot high; leaves oblong to oblanceolate, acute, sparingly toothed, ½ to 1½ inches long: heads sessile; outer involucre of two foliaceous broadly ovate opposite bracts, 3 lines long, the inner saccate, closely enclosing and conformable to the achenes, thin and somewhat reticulated, unappendaged: disk-flowers 5, sterile; ray-flowers 5, the yellowish ligule very short (½ line long or less): achenes obliquely obovate and compressed, smooth and coriaceous, a line long; pappus none. — In fields at Del Rio, State of Mexico; August, 1890 (n. 3230).

TITHONIA MACROPHYLLA. Leaves thin, scabrous above and on the veins beneath, the cauline large (about a foot long) with a broadly ovate blade cuneate from a shallow sinus and decurrent into the winged petiole, deeply 3-lobed, the lobes narrowly acuminate and serrate; uppermost leaves much smaller, ovate, not lobed: peduncles and heads sparingly pubescent; outer involucral scales foliaceous, narrowly lanceolate, acuminate, an inch long or more, the inner somewhat shorter and broader: rays orange, 1½ inches long: achenes appressed-silky, 4 lines long; pappus of two awns and a crown of six broad and very obtuse denticulate scales half as long. — Barranca, near Guadalajara; Sept., 1889 (n. 2798).

VIGUIERA LEPTOCAULIS. Annual; stem erect, slender, 3 or 4 feet high, sparingly branched and somewhat strigose above, glabrous below: leaves opposite, narrowly lanceolate, abruptly cuneate to a short petiole, attenuate upward from near the base, sparsely serrulate, very scabrous above, 4 inches long: heads solitary on the few branches; involucral scales linear-lanceolate, long-acuminate: ray-flowers sterile; ligules orange, an inch long: achenes glabrous, compressed, bearing a single caducous attenuate chaffy palea dilated and lacerate at base. — In the Sierra Madre near Monterey: July, 1888 (n. 2247).

OTOPAPPUS ACUMINATUS. Tall, scabrous: leaves opposite on slender petioles (3 to 6 lines long), ovate- to oblong-lanceolate, narrowly long-acuminate, rounded or subcordate at base, distantly glandular-serrulate, very scabrous above and scabrous-hirsute on the veins beneath, 3 to 6 inches long by ¾ to 1½ broad: heads in terminal and axillary pedunculate corymbs, broad and many-flowered, radiate, 3 lines high; involucral scales in several series, short, narrow, somewhat squarrosely tipped: ligules small (1½ lines long): achenes of the ray

3-winged, the two outer wings narrow, the inner broader, produced above and adnate to the awn of the pappus; disk-achenes compressed, similarly winged on one edge, scarcely at all on the other, the pappus reduced to the two very unequal processes at the angles: appendages of the style-branches acuminate. — Barranca near Guadalajara; October, 1889 (n. 2999.)

SPILANTHES BOTTERII. Annual, branching, about a foot high, sparingly pubescent or glabrate: leaves ovate to oblong-ovate, cuneate at base and shortly petiolate, acute or shortly acuminate, 1 or 2 inches long: peduncles slender, mostly equalling or somewhat exceeding the leaves, nearly glabrous: heads ovate-conical, 3 to 5 lines long, discoid, the glabrous narrowly oblanceolate involucral scales 2 or 3 lines long: achenes ciliate, the sides nearly glabrous, striate; pappus of two slender bristles. — Near Guadalajara; November, 1889 (n. 2946); also collected in Orizaba by Botteri (n. 825 in Herb. Gray).

SALMEA PALMERI. Stem erect, rather stout, 3 to 5 feet high or more, branching, glabrous or slightly pubescent above: leaves subcoriaceous, opposite, very shortly petiolate, ovate to ovate-lanceolate, acute or acuminate, rounded at base, distantly glandular-serrate or serrulate, strongly veined and slightly pubescent, scabrous on the margin, 2 to 4 inches long: heads 2 to 5 lines high, few to many, closely corymbose; scales acute, finely pubescent above, as also the chaff of the receptacle: corolla-tube as long as the throat, the limb deeply cleft: achenes compressed or more or less acutely 3–4-angled, short-ciliate on the angles, the sides nearly glabrous; pappus of two nearly equal attenuate bristle-like paleæ, or of three or four more unequal ones. — Near Guadalajara; n. 528 Palmer and n. 2345 Pringle (1889), both distributed through some inadvertence as *S. grandiceps*, Cass., to which they have little resemblance; also Pringle's n. 2155 and 2170 of 1889.

DAHLIA DISSECTA. Stems slender, lax, ascending from a decumbent or procumbent woody base, 1½ to 2 feet high, glabrous throughout: leaves deltoid in outline, 3 to 6 inches long, twice or sometimes thrice pinnate, the lanceolate to linear segments mostly laciniately lobed: heads long-pedunculate; outer involucral scales suborbicular, 3 lines long, the inner narrowly oblong, 6 to 8 lines long; rays purple or "mauve-colored," 1 to 1¼ inches long: achenes linear-oblanceolate, truncate, 4 lines long, nerved and with a strong central ridge on both sides, somewhat minutely pubescent on the inner surface. — On limestone ledges at San José Pass, San Luis Potosi; July, 1890 (n. 3167).

DAHLIA PUBESCENS. Stem erect from a cluster of small tubers, 1½ to 3 feet high, leafy, more or less pubescent with mostly short stiff pointed hairs: leaves pinnate, 3 to 4 inches long, the 5 to 7 leaflets (an inch long) ovate to lanceolate, coarsely and acutely toothed: heads erect on long peduncles, coarsely pubescent at base, the outer scales ovate-lanceolate, acutish, 4 or 5 lines long, the inner lanceolate, 9 lines long in fruit; rays purple, 12 to 15 lines long: achenes nearly as in the last, but usually shorter (3 lines long) and broader. — On limestone bluffs at Flor de Maria, State of Mexico; August, 1890 (n. 3164).

BIDENS DAHLIOIDES. Low and slender, glabrous, bearing tubers along the slender branches of a divided rootstock: lower or lowermost leaves entire, lanceolate or oblanceolate, acute, attenuate to the petiole; the upper (3 inches long) pinnately 3–5-lobed, the terminal segment broadly ovate to lanceolate, less deeply 3-lobed, the lateral ovate-lanceolate, entire: heads solitary upon elongated terminal peduncles, the purplish ray 1½ inches long: scales of the two involucres similar and nearly equal, many-nerved, 6 lines long: achenes oblanceolate, 5 lines long, flattened, with two short stout retrorsely bearded awns at the angles. — Dahlia-like in habit, but with the awned achenes and short-appendaged style-branches of *Bidens*. On hillsides at Flor de Maria, State of Mexico; Sept., 1890 (n. 3168).

BAHIA SCHAFFNERI. Annual, branching from the base, more or less decumbent or procumbent and strigulose-puberulent: leaves subternately decompound, the segments linear and usually short: heads about 3 lines high, the involucre of 8 to 10 broadly oblanceolate obtuse or acutish bracts: ligules deep yellow, short: achenes very narrowly obpyramidal, somewhat hispid on the angles, especially near the base, 1½ lines long or more; pappus of five obovate imbricate scales, about ½ line long, nearly equalling the slender corolla-tube. — Sandy plains near San Luis Potosi; May, 1889 (n. 3028). Also collected by Dr. Schaffner (n. 327, in part) in the same locality, and by Parry & Palmer (n. 494), referred to *B. anthemoides*. It is the same, moreover, as a plant cultivated from Mexican seeds in the Jardin des Plantes in 1838 and 1839, of which there are specimens in Herb. Gray. *B. anthemoides*, Gray, with which the species has been confused, is represented in Herb. Gray by specimens collected at Toluca by Berlandier, and by 327 Schaffner (in part), probably from the valley of Mexico; it is also 3143 Pringle, collected near the city of Mexico. As described and figured in HBK. Nov. Gen. & Spec., it is characterized by white ligules and by a much shorter and broader and more pubescent achene.

SENECIO JALISCANA. Perennial, tall and erect, rather stout, white-tomentose throughout: leaves ovate to oblong-ovate, thickish, subcordate or truncate at base, acute, sinuately and acutely few-toothed and glandular-denticulate, densely tomentose beneath, subglabrate above, 3 to 4 inches long or less: heads discoid, many-flowered, in rather dense compound corymbs terminating short peduncle-like branches which are bracteate only above; involucre short (2 lines long), of 8 or 10 imbricated scales, calyculate at base: achenes glabrous; pappus white, the somewhat rigid setæ scabrous and often thickened at the tips. — With the foliage and habit nearly of *S. sinuatus*, but the involucre and pappus of *S. barba-Johannis*. In the Chapala Mountains near Guadalajara; December, 1889 (n. 2931).

CACALIA (CONOPHORA) POCULIFERA. Nearly glabrous, puberulent above, 3 or 4 feet high, branching and naked above: leaves few, the lower long-petiolate, centrally peltate with depressed centre, 6 to 8 inches broad, deeply 7–9-lobed with narrow sinuses, the broad lobes sinuately toothed; upper leaves subreniform, lobed and decurrent into a short very broadly auriculate-clasping petiole, or cordate-ovate, sessile and coarsely and acutely toothed: heads 5-flowered on short pedicels in rather dense terminal corymbs; involucre of 5 glabrous scales, 2 lines long, slightly calyculate; receptacle flat, naked: corolla-lobes as long as the tube: achenes glabrous or nearly so; pappus fuscous. — Near Guadalajara, Jalisco; July, 1889 (n. 2879).

CNICUS VELATUS. Stem slender, erect from a tuberous-fascicled root, branched above: radical leaves linear-oblanceolate, 6 to 12 inches long by ½ to 1 broad, long-petiolate, glabrous or slightly floccose-pubescent above, white-tomentose beneath, entire with short scattered spines upon the margin or sparsely sinuate-lobed, the lobes acute and sparingly spinulose; cauline leaves sessile and decurrent, linear-lanceolate, the short lobes and auricles slightly more strongly spinulose: heads solitary on the elongated branches, campanulate, 9 to 12 lines high, the lanceolate outer scales tipped with a short appressed spine and covered by a veil of floccose hairs: flowers pale purple: anther-tips attenuate. — In low meadows, Flor de Maria, State of Mexico; August, 1890 (n. 3228).

CNICUS (ECHINAIS) LINEARIFOLIUS. Stem erect, very leafy and wing-angled, simple: leaves linear, the radical 12 to 15 inches long by an inch broad or less, petiolate, pinnately many-lobed to the middle, the broad lobes and sinuses undulately margined and spinulose, roughish above, white-tomentose beneath; the cauline similar but smaller, sessile and decurrent, acuminate, erect: heads small (9 lines high), broad, nearly sessile in a terminal cluster; outer scales shortly spinose-tipped, lanceolate, scariously dilated above, the margin entire or somewhat lacerate: corolla purple: anther-tips acuminate. — In low meadows near the city of Mexico; August, 1890 (n. 3145).

PEREZIA COLLINA. Stout and tall, glabrous or the inflorescence slightly puberulent: leaves thick and rigid, broadly oblanceolate, acute, narrowed to the sessile auriculate base, irregularly toothed, 6 to 7 inches long or less, the upper ones narrower: heads in rather close panicles terminal on the branches, 8-flowered, the narrow acuminate scales somewhat tomentose, not glandular-puberulent, the longer 5 lines long: achenes (2½ lines long) glandular-puberulent and hispidulous. — In foliage and habit very closely resembling *P. rigida* (which is collected near the same locality), differing in the narrower acuminate involucral scales, rather fewer-flowered heads, and longer hispidulous achenes. The five nearly equal long-linear lobes of the corolla are coherent into the two lips only at the tips, or are at length entirely distinct. Hills near Guadalajara; December, 1888 (n. 2123).

STYRAX JALISCANA. Leaves round-ovate to oblong-obovate, acute, at base obtuse or somewhat cuneate, white-tomentose and reticulately veined beneath, green and becoming sparsely pubescent above, 2½ to 4 inches long, on petioles 2 or 3 lines long: peduncles axillary and 1-flowered, or terminal and 2–5-flowered: calyx very shortly toothed; corolla 6 to 8 lines long, the pubescent filaments adnate to the short tube: fruit depressed-globose, valvately dehiscent, usually 3-seeded, 5 or 6 lines broad. — In the Sierra de San Esteban and on rocky hills near Guadalajara; May and November, 1890 (n. 3486 and 2978).

SCHULTESIA MEXICANA. Glabrous; stems stout, erect, 2 or 3 inches high, sparingly branched above with short erect branches, 5–9-flowered: leaves oblong-ovate or -lanceolate, sessile and clasping, 3 to 6 lines long: flowers shortly pedicellate; calyx strongly winged, nerveless excepting a stout nerve at the base of each wing, 5 lines long, not cleft to the middle, the teeth long-acuminate; wings strongly cross-veined; corolla yellowish, becoming purplish, 7 to 9 lines long: filaments not appendaged; anthers oblong, sagittate. — Damp places on the plains near Guadalajara; October, 1889 (n. 2598). Distributed as a new species of *Microcala*.

EHRETIA MEXICANA. A shrub, with the young branches tuberculate and somewhat hispid: leaves lanceolate, short-acuminate, subcuneate at base, serrate, minutely appressed-strigulose above, pubescent and reticulately veined beneath, 1 or 2 inches long on a pubescent petiole 2 to 4 lines long: flowers small, in dense compound terminal pubescent corymbs; calyx deeply cleft, ½ to nearly 1 line long; corolla white, nearly 2 lines long: fruit unknown. — At the base of the mountains near Lake Chapala; May, 1890 (n. 3085).

BOERHAAVIA OCTANDRA. Stems slender, dichotomously and divaricately branched, glabrous or puberulent above: leaves broadly ovate, acutish or abruptly short-acuminate, rounded at base, sparsely pubescent and shortly ciliate, ½ to 1¾ inches long: umbels terminal, few – many-flowered, the flowers nearly sessile; perianth tubular to funnelform with a short slightly dilated limb, green with a tinge of red, 2 lines long: stamens 8, exserted, fruit oblong, 4 lines long by 1½ broad, glabrous with a few scattered tubercles. — Much resembling *B. scandens* in habit and foliage. On river-banks near Guadalajara; October, 1889 (n. 2958).

ARISTOLOCHIA (GYMNOLOBUS) NANA. Stems procumbent, from a slender subterranean branching rhizome, slender and flexuous, 3 to 6 inches long, leafy, nearly glabrous: leaves from reniform-cordate to deltoid-cordate, very obtuse or acutish and with broad rounded basal lobes, 3 to 8 lines long, on short petioles: flowers solitary in the axils, nearly sessile; ovary pubescent, narrow, 2 lines long; perianth dark brown, narrowly tubular and nearly straight, 1½ to 2½ inches long, the elongated narrow blade exceeding the tube, the scarcely dilated base of the tube closed by a glabrous diaphragm with a circular central orifice: anthers 5: capsule depressed-globose, 6 lines broad. — Collected by Prof. A. Dugès of Guanajuato in 1883 at Guadalcazar in the State of San Luis Potosi, and by Mr. Pringle in August, 1890 (n. 3630), on dry limestone hills at San José Pass in the same State.

PIPER (ENCKEA) JALISCANUM. Shrubby, 8 feet high, glabrous: leaves oblong-ovate to round-ovate, acute or short-acuminate, abruptly short-cuneate at base, 5–7-nerved, 1½ to 3 inches long, on slender petioles 3 to 7 lines long, not punctate, becoming thickish, rather rigid and glaucous: spikes slender, on peduncles nearly equalling the petioles, 9 to 15 lines long, becoming 2½ inches long in fruit, densely flowered: flowers 6-androus: fruit sessile, oblong, obtusely quadrangular, a line long. — Cañons near Guadalajara, in dense moist shade, Dr. E. Palmer, June, 1886 (n. 122), in flower, and Mr. C. G. Pringle in December, 1888 (n. 2153), in young fruit.

PEPEROMIA JALISCANA. Herbaceous, the short stem from a small tuberous root, glabrous: leaves 2 to 4, one radical, the rest cauline and alternate, suborbicular, cordate at base, very obtuse or rounded at the summit, thin, 2 to 5 inches broad, on petioles 6 to 12 lines long or more: spikes 2 to 4, axillary and terminal, pedunculate, slender and elongated (4 inches long or less): flowers scattered, sunk in pits in the fleshy rhachis: bract very minute and fleshy: stamens two, scarcely exserted: ovary oblique-ovate, the stigma apical and sessile. — On rich shaded banks in the barranca near Guadalajara; September, 1889 (n. 2953).

Euphorbia (Cyttarospermum) digitata. Near *E. dioscoreoides*, probably annual and 2 feet high, erect, with rather numerous very slender ascending branches, glabrous: rameal leaves about equalling the very slender petioles, ovate-lanceolate, acute, rounded at base, 6 to 9 lines long, gradually diminishing upward, basally peltate, entire, ciliate; peduncles solitary in the axils (rarely in pairs), usually exceeding the leaves, binodose and glandular-bracteate (bracts very rarely filiform), bearing only a single terminal involucre: involucres turbinate-campanulate, $\frac{2}{3}$ line long; appendages of the roundish glands regularly 4–6-parted into narrowly linear segments, or these sometimes more or less united: capsule long-exserted: seeds $\frac{3}{4}$ line long, ovate, pitted, the pits with a central cavity and their margins rather obscurely tuberculate. — On limestone hills near Las Palmas, San Luis Potosi; October, 1890 (n. 3525). Distinguished from *E. dioscoreoides* by its habit, less pubescence, solitary glandular-bracteate peduncles and more divided appendages. The seeds are also smaller, scarcely more than half as large, similarly pitted, but the margins of the pits less distinctly tuberculate.

Euphorbia (Cyttarospermum) subpeltata. Perennial, the stems somewhat woody from a thickened or subtuberous root, erect, glabrous, with numerous ascending or divaricate branches: leaves alternate, on very slender petioles (3 to 8 lines long), semi-orbicular, short-cuneate at base and attached to the petiole slightly within the margin, entire, glabrous, 3 to 8 lines broad: involucres in short slender axillary racemes, with elongated filiform bracts, campanulate, $\frac{1}{2}$ line long; lobes minute, lacerate; glands very small, subreniform, the purple or purplish appendages palmately divided into 3 or 4 linear-subulate obtuse lobes as long as the involucral tube: capsule glabrous, the subglobose greenish seeds ($\frac{2}{3}$ line long) marked with broad shallow pits and somewhat tuberculate. — On limestone ledges in Tamasopo Cañon, San Luis Potosi; August and September, 1890 (n. 3272). Nearly allied to *E. dioscoreoides*.

Euphorbia (Tithymalus) misella. Annual, erect, branching alternately below, dichotomously above, low and slender (2 or 3 inches high), slightly pubescent: lower leaves alternate, the upper opposite, petiolate, round-obovate, entire, 1 or 2 lines long: involucres solitary in the forks, pedunculate, scarcely ¼ line long, the lobes fimbriate, the glands (3 or 4) broadly stipitate, minute, rounded, entire: capsule smooth, ⅓ line long: seed ovate, smooth or very obscurely indented, ecarunculate. — On wet grassy borders of prairie ponds, Flor de Maria, State of Mexico; October, 1890 (n. 3305). Not nearly related to any other of our species of the section.

PHYLLANTHUS PRINGLEI. A small tree (15 feet high), with smooth gray bark on the numerous branches, and the slender herbaceous branchlets sulcate-angled: leaves distichous, thin, round-ovate to orbicular or round-obovate, acutish or usually obtuse or retuse at the summit, as also at base, 6 to 12 lines long or less, on petioles about a line long; stipules short, obtuse and scarious: pistillate flowers solitary (or only 2 or 3) in the axils, on very slender pedicels 2 to 5 lines long; calyx 6-parted, the oblong segments nearly equal; disk cupulate; styles bifid, spreading: staminate flowers and fruit unknown. — On limestone ledges at Las Palmas, San Luis Potosi; June, 1890 (n. 3532). The material is insufficient for a full description, but it seems quite unlike any known species that is likely to be found in Mexico.

CROTON (EUCROTON) CALVESCENS. Shrubby, herbaceous above, the young branches and leaves densely covered with a white or grayish stellate tomentum, soon glabrate and more or less scabrous with a rigid substellate puberulence: stipules obsolete; leaves ovate to ovate-lanceolate, acuminate, rounded and biglandular at base, serrulate, 2 or 3 inches long on petioles 3 to 12 lines long: racemes terminal, sessile, 3 to 9 lines long, dense, pistillate at base; pedicels a line long: stamens 9 to 12; calyx-lobes of pistillate flowers deltoid, obtuse, not becoming reflexed: ovary densely stellate-pubescent and hispid; styles once divided; capsule becoming nearly glabrous, ellipsoidal: seed smooth and shining, 2½ lines long. — Collected by Dr. E. Palmer in 1886 (n. 706) near Chapala, Jalisco, and by Mr. Pringle in November, 1890, on hillsides near Patzcuaro in Michoacan (n. 3346). Near forms of *C. flavus*.

CROTON (EUTROPIA) ELÆAGNOIDES. A shrub or small tree, 10 to 15 feet high: leaves 3–5-nerved at base, eglandular, ovate to lanceolate, acutish to acuminate, green above and roughish with a slight scurfy puberulence, white beneath with a dense compact lepidote coating (as also the inflorescence and fruit), ¾ to 2 inches long, short-petiolate: racemes becoming 4 to 6 inches long, pistillate below; staminate flowers nearly 3 lines broad, with narrowly lanceolate acutish pubescent petals and about 15 stamens; pistillate flowers scattered, the sepals oblong or oblong-obovate, acutish, 2 lines long: styles thrice dichotomous; capsule depressed, 2½ lines broad: seeds triangular-ovate, minutely and irregularly pitted. — At Las Palmas, San Luis Potosi; June, 1890 (n. 3080).

MANIHOT PRINGLEI. Apparently herbaceous, glabrous: leaves long-petioled, 5-parted to the base, the divisions 3 or 4 inches long, narrowly lanceolate or oblong-lanceolate, very acutely short-acuminate, usually obtusely lobed by a more or less broad and deep sinus on each side, glaucous beneath; stipules caducous, small and subulate; bracts of the long-pedunculate corymbose raceme foliaceous, narrowly lanceolate and acuminate, denticulate, 6 to 12 lines long: pedicels erect, usually bearing a bractlet or two: perianth of the staminate flowers glabrous, campanulate, 6 to 9 lines long, cleft nearly to the middle, the lobes valvate; stamens 10; disk large, 5-lobed; pistillate flowers narrower, the calyx 5-parted; disk conspicuous, entire: fruiting peduncles 2 inches long or more, erect; capsule glabrous, 8 lines long. — On limestone hills at Las Canoas, San Luis Potosi; July, 1890 (n. 3558). Somewhat resembling *M. Carthaginensis*.

ACALYPHA DISSITIFLORA. Perennial, herbaceous, slender, a foot high or more, diœcious, the fertile plant branching above, the staminate simple above the base, pubescent: leaves thin, ovate, 3–5-nerved, acute or shortly acuminate, rounded at base, serrate, somewhat appressed-hairy, 1 to 1½ inches long on slender petioles 3 to 6 lines long: spikes axillary, very slender, pedunculate, 1 or 2 inches long, the staminate very rarely with a pistillate flower at base, the pistillate with flowers much scattered; bracts 1-flowered, scarcely a line high, acutely 5–7-toothed, shorter than the pubescent capsule: styles short, pectinately divided. — On limestone ledges in Tamasopo Cañon, San Luis Potosi; July, 1890 (n. 3083). A strongly marked species, in Mueller's arrangement falling near *A. elliptica*.

ACALYPHA MULTISPICATA. Perennial, herbaceous, the numerous stems simple, about a foot high, pubescent with recurved woolly hairs; diœcious: leaves subsessile, 3–5-nerved at base, the lower ovate or obovate and obtuse or acute, the upper lanceolate and acute, serrate, strigose-pubescent, 1 or 2 inches long: spikes pedunculate in nearly all the axils, the staminate slender, dense, ½ to 1 inch long, the pistillate short and mostly few- (1–10-) flowered; bracts 1-flowered, reniform, acutely 7–11-toothed, becoming 2 or 3 lines long: styles pectinately divided; capsule pubescent. — On hillsides near Guadalajara; July, 1889 (n. 2903). In the same group with the last species.

Acalypha flavescens. A shrub 5 to 10 feet high, the young branches and petioles somewhat pubescent: leaves thin, 3–5-nerved, ovate to ovate-lanceolate, rounded at base, acuminate, serrate, very minutely puncticulate and finely rough-puberulent, 3 to 4 inches long on petioles 1 to 1½ inches, on the short fruiting branchlets smaller and nearly sessile; stipules rigidly setaceous from a broad base: spikes sessile, 1 to 1½ inches long, the staminate axillary, dense, the pistillate terminal and rather loose; bracts small, 1-flowered, thin and loose, broadly reniform, many-nerved, 7-toothed, the teeth attenuate above: styles sparingly pinnatifid; ovary densely pubescent. — In Tamasopo Cañon, San Luis Potosi; June, 1890 (n. 3073). Near *A. carpinifolia* as grouped by Mueller.

Acalypha (Linostachys) longipes. Suffrutescent, the young herbaceous branches sparsely pubescent: leaves thin and glabrous or slightly hispid on the nerves, 3–5-nerved at base, oblong-lanceolate to lanceolate, acuminate, subcordate at the narrowed base, serrulate, 1 or 2 or sometimes 4 inches long, on pedicels 1 to 9 lines long; stipules attenuate-subulate: staminate spikes axillary, sessile, 3 or 4 inches long; pistillate racemes pedunculate, axillary, very slender, 2 to 5 inches long, the pedicels solitary or in pairs and unequal, the longer 1 to 12 lines long; bracts minute: ovary densely muricate. — On limestone ledges in Tamasopo Cañon, San Luis Obispo; June, 1890 (n. 3082).

Sebastiania Pringlei. A glabrous shrub with slender branches, diœcious or the sterile aments with sometimes (?) a pistillate flower at base: leaves rather thin, on short slender petioles, from elliptical and obtuse to lanceolate and acute or short-acuminate, rounded or subcuneate at base, eglandular, obsoletely crenate-serrate, 9 to 18 lines long: spikes terminal, nearly sessile; staminate bracts very short, broad and abruptly apiculate, 2-flowered; flowers nearly sessile, diandrous; calyx of 1 to 3 minute distinct linear acuminate sepals: distillate spike 2-flowered, the upper flower usually retarded in development or abortive: bract thicker, biglandular: capsule glabrous, 4 lines long, chartaceous, dehiscing dorsally and ventrally; seed not seen. — In rocky gulches at San José Pass, San Luis Potosi; July, 1890 (n. 3136, distributed as *Gymnanthes Pringlei*). An evidently closely related species, but with much larger leaves, recently collected by Dr. Palmer near Alamos in Sonora, has nearly globose seeds with a very minute caruncle. The presence of this caruncle has determined the reference of the present species to the genus *Sebastiania*, with which in other respects the characters accord very satisfactorily. Some specimens that were received from Prof. A. Dugès, as collected by Prof. José Ramirez on the banks of the Alamos River in Sonora, closely resemble Mr. Pringle's specimens excepting that the spikes are all bisexual, the staminate bracts 4–5-flowered, and the stamens 2 or 3. The few loose seeds which accompanied these specimens show, however, no caruncle, though otherwise like those of Dr. Palmer. It is probable that this is a third species of the same genus, and that too much weight has been given to the presence of a caruncle as a generic character. The fruit of the Sonora plant is said by Ramirez to be that in which the *Carpocapsa saltitans* is found; and this is certainly true of Dr. Palmer's species. Doubtless the "jumping beans" are the product of more than one of these nearly allied shrubs. The fruit of *Sebastiania bilocularis* is found to be attacked by a similar insect, though of a different genus, which has been named by Mr. C. V. Riley *Grapholitha Sebastianiæ*. The capsules which Dr. Palmer collected, like those of the other collections, have the cocci dehiscing nearly to the base, and the rather thin valves become more or less contorted. In fruit occupied by the *Carpocapsa*, such as I have seen, the cocci remain closed, but the walls are chartaceous and complete dehiscence is readily effected.

FICUS (UROSTIGMA) JALISCANA. Young branches, buds and petioles pubescent: leaves coriaceous, round-cordate with broad more or less overlapping basal lobes, acute, 3–5-nerved at base, 3 to 4½ inches long, on petioles nearly as long, soon glabrate above and smooth though minutely puncticulate, more puberulent beneath, especially on the nerves: fruit in pairs, on stout pedicels 2 or 3 lines long, globose, densely tomentose, 4 or 5 lines broad, subtended by a broad somewhat 3-lobed involucre; fertile flowers pedicellate, with unequal sepals, one cucullate, the others shorter, broad and concave, the style rather short and stigma subcapitate; abortive pistillate flowers similar but smaller and sessile, the style elongated and stigma bifid; staminate flowers not found: orifice of the receptacle closed within by several rows of rigid closely imbricated broad bracts. — On cliffs near Guadalajara; December, 1889 (n. 2932).

FICUS (UROSTIGMA) PRINGLEI. Young branches and petioles densely pubescent with spreading hairs: leaves ovate, 3-nerved and slightly cordate at base, obtuse or acutish, 2 to 4 inches long by 1½ to 3 broad, on stout petioles 2 to 4 lines long, very rough above with fine hispidulous reticulations and prominently puncticulate, pubescent and strongly reticulated beneath: fruit sessile in pairs in the axils, involucrate with two opposite orbicular silky-pubescent bracts, globose, finely pubescent, 4 or 5 lines broad, the orifice somewhat umbonate and closed by numerous rows of imbricated rigid bracts; flowers shortly pedicellate, the pistillate with short style and nearly equal concave petals, the staminate with two strongly cucullate sepals and a broad obtuse nearly sessile anther. — In the barranca near Guadalajara; December, 1889 (n. 2928).

FICUS (PHARMACOSYCE) GUADALAJARANA. Young branches sparsely pubescent: leaves coriaceous, pinnately veined, oval, acutish at each end, 2 to 4½ inches long by 1 to 2¼ broad, on pubescent petioles 3 to 8 lines long, very scabrous above, reticulately veined beneath, and rather soft-pubescent especially on the prominent veins: fruit solitary, on peduncles 4 lines long, globose, very shortly stipitate and with a very narrow undulate involucre, 6 to 9 lines in diameter; the bracts within the orifice linear and strictly inflexed, rufous; staminate and gall-producing flowers on rather slender bracteate pedicels, the fertile nearly sessile; sepals of the staminate flower 4, broadly elliptical, the 2 nearly sessile anthers ovate-elliptical, obtuse; sepals of the pistillate flower linear, acuminate; bracts and sepals rufous. — In the barranca near Guadalajara; October, 1889 (n. 2947). The galls were found occupied by a black winged insect, — the only instance in which I have detected the gall-fly in any of our species, though doubtless often present. Mr. Riley informs me that he finds in this same fruit gall-insects of three different genera.

FICUS (PHARMACOSYCE) RADULINA. A tree with rather stout finely pubescent branchlets: leaves thin-coriaceous, oblong-lanceolate, acute or short-acuminate, 3–5-nerved and acutish at base, very minutely roughish-punctate above becoming smooth, glabrous beneath, 3 to 6 inches long by 1½ to 2¼ broad, on petioles 8 to 16 lines long: fruit slightly pubescent becoming glabrous, obovate-globose, 10 lines broad, involucrate with 3 short-deltoid deciduous bracts, solitary, on peduncles 2 or 3 lines long; orifice somewhat prominently margined, closed by numerous intruded narrowly linear bracts: staminate flowers pedicellate, with deeply 4–5-cleft perianth, the lobes lanceolate, acute; stamens 2 or sometimes 1, the anthers elliptical, obtuse; pistillate flowers sessile or pedicellate, 4–5-parted, the sepals narrowly linear. — Collected by Dr. Edward Palmer at Hacienda San Miguel near Batopilas in southwestern Chihuahua, in 1885 ("L."), and again in March, 1890 (n. 367), at Alamos in Sonora. The species much resembles *F. radula* and *F. anthelmintica.* In the fruit examined an apparently perfect flower was occasionally found, perhaps however only pseudo-hermaphrodite, as in the few East Indian species of which

Dr. King forms his section *Palæomorphe*, based upon this characteristic mark.

Ficus fasciculata, Watson, Proc. Am. Acad. 24. 78. This species was described from specimens in quite young fruit, found in cultivation at Guaymas, but said to be native in the same region. A very similar, if not the same, species has been recently found by Mr. Pringle (n. 3551) in Tamasopo Cañon in the mountains of San Luis Potosi, and this appears to be identical with what was collected by Ervendberg (n. 332) near Tantoyuca in Huasteca, and by Botteri still farther southward in Orizaba. The leaves, however, vary considerably in size, and from obtuse to quite sharply acuminate, and the only specimen seen by Mr. Pringle was a small erect shrub very different in habit from those at Guaymas as described by Dr. Palmer. The orifice of the small thin fruit is in the Guaymas specimens much impressed, while in the others it is conspicuously prominent, which may be due to the stage of growth. All may possibly be referrible to *F. sapida*, Miquel, of Costa Rica and Panama, as forms of one polymorphous species.

Pilea glabra. Low and herbaceous, glabrous: leaves thin, showing on the upper side numerous linear cystoliths, entire, lanceolate or broadest near the middle and narrowed each way, acutely acuminate, rounded at the very base, 3-nerved, the nerves continued to the apex, 2 to 4 inches long by 8 to 16 lines broad, on petioles an inch long: panicles pedunculate, very loose and slender, exceeding the petioles, solitary or in pairs in the axils, androgynous. — In Tamasopo Cañon, San Luis Potosi; August, 1890 (n. 3550).

Myriocarpa brachystachys. Young branches, petioles and lower surface of the leaves densely tomentose: leaves ovate, rounded at base, short-acuminate, acutely serrate, finely bullate, nearly glabrous above, 3 or 4 inches long, on petioles ½ inch long: pistillate inflorescence sparingly branched, nearly sessile, the longer spikes 3 to 5 inches long, very densely flowered: sepals lanceolate, sparingly ciliate, a third as long as the sparsely hispid ovary. — In the barranca near Guadalajara; May, 1888 (n. 3021).

Juglans Mexicana. Foliage as in *J. nigra*, but with the pubescence nearly of *J. cinerea*: fruit large, subcompressed-globose, 2¼ inches high by 2 inches broad; nut 1½ inches broad, very obtusely rugose, obtuse or slightly apiculate. — On hills at San José Pass, San Luis Potosi; October, 1890 (n. 3322).

Microstylis (Dienia) tenuis. Stem slender from a small tuberous base, 4 to 6 inches high, with a single narrowly ovate acutish basal sheathing leaf 1½ inches long: flowers greenish ochroleucous, in an open raceme 2 inches long; pedicels very slender, 1 to 3 lines long; bracts very small: sepals and petals linear-lanceolate, acuminate, 2 lines long, the lip a little shorter, attenuate from a broader base. — In low meadows, Flor de Maria, State of Mexico; July, 1890 (n. 3186).

SPIRANTHES PRINGLEI. Root of fascicled fusiform tubers an inch long; stem slender, 4 to 8 inches high, puberulent, the scattered sheathing bracts (5 or 6) thin, acute or acuminate, ½ to 1 inch long: spike loosely few-flowered, 1 or 2 inches long, the narrowly lanceolate bracts equalling the ovaries: flowers white, the lanceolate sepals 3 lines long; lip a little longer, dilated above into a reniform undulately margined blade; column short, its crest short and obtuse; beak of the anther oblong, acutish: capsule oblong-ovate, 3 lines long. — Moist plains near Guadalajara; June, 1889 (n. 2577). Radical leaves unknown.

SPIRANTHES (STENORHYNCHUS) JALISCANA. Radical leaves unknown; stem from a fascicle of long tuberous roots, leafless, a foot high, glandular-pubescent above, partially covered with acute or short-acuminate bracts an inch long: flowers in a rather loose slender spike, subtended by linear-lanceolate acuminate bracts 4 to 6 lines long; sepals and petals red, 9 lines long, narrow above the prominent gibbosity, acuminate, the lip much narrowed above the dilated and auricled basal portion: capsule ½ inch long. — Plains near Guadalajara; June, 1889 (n. 2874). Related to *S. speciosa*.

BLETIA PALMERI. Stem from a tuberous-thickened base upon a slender rootstock, slender, 1 to 1½ feet high, 6–12-flowered: leaves shorter than the stem, broadly linear, 6 to 10 inches long by 3 to 6 lines broad; bracts small: perianth purplish, 6 to 9 lines long; sepals and petals nearly equal, oblong, acutish; lip 6 lines long and nearly as broad, with broad rounded lateral lobes, a rhomboidal middle lobe, and seven very prominent contiguous laminæ extending from the base to the apex: capsule an inch long, on a pedicel 3 or 4 lines long. — Collected at Rio Blanco, Jalisco, in August, 1886, by Dr. E. Palmer (n. 336), and in the barranca near Guadalajara in May, 1889, by Mr. Pringle (n. 3023).

GOVENIA ELLIPTICA. Basal sheaths very broadly dilated, the longer 6 inches long; leaves lanceolate above the enclosed petiole, acuminate, 8 inches long by 3 broad, nearly equalling the loose but many-flowered spike; floral bracts lanceolate, acuminate, shorter than the slender ovaries: sepals and petals brown, 6 lines long, bilabiately divergent, the lower sepals falcate and rather narrow, the upper oblong; lip yellow, elliptical with cuneate base, obtuse or emarginate, 3 lines long. — Cool rich cañons in the mountains near Monterey, San Luis Potosi; June, 1890 (n. 2797).

ARETHUSA GRANDIFLORA. Flowering stem leafless from a tuberous base (6 to 8 lines in diameter), 6 to 8 inches high, with 2 to 4 very short closely sheathing bracts; foliar stem contiguous, sheathed below and bearing two long-acuminate narrow leaves (6 to 12 lines broad) exceeding the scape: flower solitary, large, the unguiculate sepals oblong-lanceolate, acuminate, falcate, 15 lines long; lip 2 inches long or more and 1½ broad, purple, 3-lobed, erosely denticulate; column shorter than the sepals: ovary slender, 8 lines long. — Banks of cañons near Guadalajara; October, 1889 (n. 2997). The condition of the flowers prevented an examination of the andrœcium, but there seems no reason to doubt the correctness of the generic reference.

POGONIA (TRIPHORA) MEXICANA. Stem 2 to 4 inches high from a small tuber, sheathed at base and bearing 4 or 5 sessile leaves, the lower round-ovate, acute, about 6 lines long, the uppermost lanceolate: flowers 2 or 3, pedicellate, soon recurved; perianth 5 lines long, the greenish sepals and white petals linear, acute; lip purplish above, with three green median nerves, cuneate to a short broad claw, 3-lobed, the middle lobe subdeltoid, undulate-margined: column 3½ lines long. — In Tamasopo Cañon, San Luis Potosi; August, 1890 (n. 3557). Resembling *P. pendula*, and probably the same as Parry & Palmer's plant from the same region, mentioned by Mr. Hemsley as in Herb. Kew.

HABENARIA FILIFERA. Low, from a small oblong-ovate tuber, glabrous, 4 to 8 inches high: leaves erect, longer than the internodes, oblong-ovate or the lowest ovate, acute, mostly sheathing at base, 1 to 1½ inches long; floral bracts foliaceous, acuminate, nearly equalling the flowers: spike loosely rather few-flowered, 2 or 3 inches long: sepals acute, the lower oblong-ovate and subfalcate, the upper suborbicular, 2 lines long; petals bifid, the upper lobe oblong, falcate, nearly equalling the upper sepal, the lower filiform, 3 lines long or more; lip 3-lobed, the lobes all filiform, the lateral 4 lines long, exceeding the somewhat broader middle one; spur 7 or 8 lines long, acute, a little enlarged toward the end. — On moist grassy slopes, Flor de Maria, State of Mexico; July, 1890 (n. 3187). This was also previously collected by Mr. Pringle in Chihuahua in 1887 (n. 1375^b), distributed as *H. Guadalajarana*, var (?). It differs from that species in the fewer flowers, the longer lower lobes of the petals, the longer and narrower lobes of the lip, and the longer acuminate spur.

HECHTIA PEDICELLATA. Leaves long-attenuate from the base, about 2 feet long and 1½ inches broad at base, white-scurfy beneath, less so above, spinose on the margin: flowering stem flexuous, 2 or 3 feet high, covered by numerous thin lanceolate attenuate bracts serrulate on the margin: panicle glabrous, long and narrow, the numerous spreading branches about 2 inches long, mostly simple: flowers numerous, scattered, racemose; sepals and petals small, deltoid, persistent, the latter 1½ lines long: capsules oblong-ovate, 4 or 5 lines long on pedicels 2 or 3 lines long. — On ledges in the barranca near Guadalajara; October, 1889 (n. 2970).

TILLANDSIA (ANOPLOPHYTUM) PRINGLEI. Basal leaves (15 to 20 or more) abruptly convolute-linear from a dilated base (1½ inches long by an inch broad), densely lepidote with appressed centrally punctate scales, 6 to 8 inches long, recurved, the cauline shorter and soon reduced to sheathing oblong acuminate or acute lepidote bracts 12 to 6 lines long: flowering stem nearly 2 feet high, very sparingly branched; spikes 4 or 5 inches long, 6–8-flowered, glabrous, slightly flexuous; calyx little exceeding the acutish narrow appressed bract and about equalling the internodes, 7 to 9 lines long; petals long-exserted. — At Las Palmas, San Luis Potosi; June, 1890 (n. 3530).

TILLANDSIA (PLATYSTACHYS) CYLINDRICA. Basal leaves unknown; peduncle stout, a foot long or more, covered with numerous imbricated erect scurfy-canescent leaves with dilated base 1½ inches broad and attenuate upward into an elongated convolute-linear termination a foot long: inflorescence scurfy-canescent, cylindrical, 8 to 10 inches long and over 2 inches broad, of numerous (20 to 30) distichous sessile ovate-lanceolate 8–10-flowered spikes which are 2 or 2½ inches long and an inch broad; bracts tinged with red on the margins, those on the rhachis more or less attenuate and the lower often much exceeding the spike, those of the spike acute, carinate, 1 to 1¼ inches long: calyx more or less scurfy, an inch long; petals greenish, 1¾ inches long, convolute below into a tube as long as the calyx; stamens and style exceeding the petals. — From Guanajuato, Mexico; Prof. Alfred Dugès. Near *T. Dugesii*.

SISYRINCHIUM PLATYPHYLLUM. Perennial, glabrous; stem stout, nearly 2 feet high, branching above, broadly winged: leaves ensiform, acute, 6 or 8 inches long by 6 to 9 lines broad, smooth on the margin, the uppermost lanceolate; floral bracts equal, broad, acute, 1¼ inches long; pedicels slightly exserted: ovary small, subpuberulent: perianth yellow, the segments oblong, obtuse, 9 lines long by 3 broad, faintly nerved except toward the base: free portion of filament nearly 2 lines long; style cleft nearly to the base. — In the barranca near Guadalajara; July, 1889 (n. 2876). Resembling *S. Arizonicum*, but more glabrous, the broader leaves less acuminate, and the style more deeply cleft; fruit unknown.

AGAVE (LITTÆA?) HARTMANI. Acaulescent; leaves very numerous in a dense rosette (becoming a foot in diameter), broadly linear above the short dilated base, the blade 3 inches long by about ½ inch broad, very thick, convex on the back, marked on both sides by broad intersecting gray lines (as in *A. filifera*), ending abruptly in a stout brown spine 2 or 3 lines long, the margins at base acute and finely serrulate, obtuse above and bearing on each side about half a dozen very slender recurved ash-gray threads: flowers and fruit unknown.— Collected by Mr. C. V. Hartman, botanist of the Lemholtz expedition, and in cultivation at the Cambridge Botanic Garden.

AGAVE (MANFREDA) BRUNNEA. Acaulescent: leaves rather few, fleshy, recurved, channelled above, 4 inches long or less by 6 to 10 lines broad in the middle, the margin armed with scattered broad hooked spines a line long: flowering stem 2 feet high, with lanceolate narrowly attenuate bracts shorter than the nodes: flowers few (about 6), sessile; ovary 6 lines long; perianth 15 to 18 lines long, the narrow tube nearly twice longer than the dark brown narrowly oblong spreading lobes: stamens and style much exserted: capsule broadly ellipsoidal, about 9 lines long. — On the battle-field of Buena Vista, Tamaulipas; July, 1888 (n. 2218).

ECHEANDIA NODOSA. Roots coarsely fibrous; the base of the plant surrounded by the more or less fibrous remains of numerous dead leaves: leaves broadly linear, 18 inches long by 12 to 15 lines broad, attenuate to each end, very shortly ciliolate: stem 3 feet high, paniculately branched, the branches spreading and very slender with numerous nodes (mostly approximate, 3 to 6 lines apart, sometimes more distant); pedicels very slender, 3 to 6 lines long, jointed a little below the middle: perianth pale yellow, 5 lines long: capsule broadly elliptical, 2 or 3 lines long. — In the barranca near Guadalajara; Nov., 1888 (n. 2151). This genus must include several species, though it is difficult to identify the forms that have been described as distinct, and which have of late all been embraced under *E. terniflora*. A form more nearly resembling typical *E. terniflora* is Mr. Pringle's n. 3183 of 1890. This has long and more or less tuberous-thickened roots, and linear-lanceolate leaves attenuate from near the base to a narrowly acuminate apex (4 to 8 inches long by 9 to 18 lines broad), more distinctly ciliate: branches less slender, ascending, with distant nodes; pedicels jointed toward the base; perianth yellow becoming pale, 5 or 6 lines long, and capsule 3 or 4 lines long. Both of these species must be distinct from the common form with very elongated and narrow leaves.

Dasylirion inerme. Tree-like, 20 to 30 feet high and 2 to 4 feet thick at base, with few branches: leaves 2 to 4 feet long by 6 lines broad, long-attenuate, thin and scarcely at all carinate, the margin unarmed, very minutely serrulate: inflorescence paniculate, a foot broad or more: fruit triquetrous, broadly winged, 5 or 6 lines long. — On limestone ledges at Las Palmas, San Luis Potosi; June, 1890 (n. 3108). A very remarkable species.

Tradescantia Pringlei. Stems slender, decumbent and rooting at base, glabrous or with a pubescent line on one side: leaves ovate, short-acuminate or only acute, 1 to 1¾ inches long, minutely puberulent, the short petiole and loose sheath villous-ciliate: peduncles axillary and terminal, a little shorter than the leaf, bearing a small head of nearly sessile flowers: bractlets and sepals glabrous or a little ciliate, the latter 2½ lines long; petals purple: stamens 6, unequal, the longer with filiform filaments bearded in the middle (or one naked) and broadly oblong anthers, the shorter filaments very densely bearded in the middle with green gland-tipped hairs, the anthers orbicular; anther-cells contiguous. — In the Sierra Madre near Monterey; July, 1888 (n. 2226).

Chamædorea Pringlei. Acaulescent or nearly so: leaves erect, pinnate, nearly 3 feet high; leaflets 12 to 15 on each side of the triangular rhachis, linear-lanceolate, acuminate, 6 or 8 inches long by 3 or 4 lines broad: inflorescence diœcious, the staminate spadix arising from the base and about equalling the leaves, simple; peduncle covered with sheathing bracts; flowering rhachis about 8 inches long: flowers scattered; calyx 3-parted, the segments orbicular; corolla 3-parted, valvate; abortive ovary columnar, greenish: pistillate flowers and fruit unknown. — In Tamasopo Cañon, San Luis Potosi; June, 1890 (n. 3527). The most northern locality known for any species of the genus. While the absence of pistillate flowers renders the section to which the species belongs uncertain, it nevertheless appears to be clearly distinct from the few other known species that have a simple spadix.

Eriocaulon Jaliscanum. Dwarf: leaves subulate, acuminate, 5 to 8 lines long by nearly a line broad, little exceeding the bifid sheaths: scapes very slender, $\frac{1}{2}$ to 3 inches high; heads globose to oblong-ovate, $\frac{1}{2}$ to $1\frac{1}{2}$ lines high; involucral bracts scarious, white or nearly so, oblong to obovate, obtuse, the inner white becoming somewhat fuliginous, acutish: flowers trimerous, mostly pistillate, a few at the apex staminate; petals linear-spatulate, slightly ciliate above: seeds very minutely papillose. — Wet places near Guanajuato; November, 1889 (n. 2936).

3. *Upon a wild Species of* Zea *from Mexico.*

Prof. W. H. Brewer, in a communication to Dr. Sturtevant, to be found in the paper of the latter upon "Indian Corn" in the Report of the New York State Agricultural Society for 1878, gives a statement which Roezl, the well known German collector, made to him in 1869 to this effect: that "he found in the State of Guerero a *Zea* which he thinks specificially distinct, and he thinks undescribed; the ears very small, in two rows truly distichous; the ear (but not each grain separately) covered with a husk, the grain precisely like some varieties of maize, only smaller and harder." Specimens of a *Zea* which is in all probability the same that Roezl referred to were received by me in 1888 from Prof. A. Dugès of Guanajuato under the designation of *Maïs de Coyote*. It was reported to him as growing wild at Moro Leon, to the south of the State of Guanajuato, and as not at all resembling ordinary varieties of maize. The specimens sent were two very slender stalks about four feet high, with a small terminal staminate inflorescence but no trace of fertile spikes. These were probably very depauperate stalks, that had been selected for easy carriage. Accompanying them was a united cluster of about half a dozen small ears enveloped in their husks, each about two inches long and bearing a few rows of small white pointed kernels.

Some of the peculiarities of this remarkable corn were noted at the time, but nothing more was done until last year, when an attempt was made to grow it at the Botanic Garden, Cambridge, with quite unexpected results. The corn was planted early under glass, and as soon as danger from frosts was over the plants were transferred to a warm sunny location, where they soon began to grow vigorously and to send out numerous offshoots from the base. These "suckers" grew as rapidly as the main stalk, so that the plants, which had fortunately been placed some feet apart, had the appearance of two "hills," one of the two having nine and the other twelve stalks ascending from a common base. The tallest were over ten feet in height, with a diameter of nearly two inches, and they would have become yet taller had the season permitted. Their foliage and pubescence were in every way as in ordinary field corn, the staminate tassels with conspicuously longer and more drooping racemes, the habit of growth wholly unusual. In our ordinary form the erect culm is always apparently single, bearing solitary axillary ears which are terminal upon a usually short leafy-bracted peduncle. This peduncle is in fact a lateral branch, bearing a terminal pistillate spike corresponding to the staminate panicle on the main stem. In this Mexican corn, on the other hand, the better developed stalks were evidently branched from several of the axils, the branches often becoming three or four feet in length, very leafy, and having at least a rudimentary ear in the axil of every leaf. Several, sometimes half a dozen, perfect ears were formed upon each branch. The terminal ear was always androgynous, staminate at the summit. On the shorter stems the branches were reduced to a more or less crowded axillary cluster of ears similar to the one received from Prof. Dugès. The last year's season was a long one, and there was no heavy frost in Cambridge until near the end of October. The corn however was at that time still very green, and the stalks were finally cut and stored under shelter in the hope that the ears would ripen in the stack; but upon very few did any of the kernels mature.

The natural supposition was that we had here at last the original wild state of our cultivated maize. A careful comparison of the two, as thorough as the material at hand of the cultivated forms would permit, has led me first to doubt the probability of this, and now to consider the form in question a distinct species. The differences upon which this conclusion is based are in the habit of growth, the arrangement of the staminate spikelets and the nervation of their glumes, the form of the glumes of the pistillate flowers, and the ready disarticulation of the ripened ear.

It appears from descriptions, figures, and such specimens as I have seen of cultivated maize, that the staminate spikelets are in pairs at the joints of the rhachis, and their empty glumes 7–9-nerved. In the Mexican plant there are usually three and sometimes four together, one of them short-pedicelled, the others more nearly sessile. The empty glumes are 3–5-nerved and bicarinate, the flowering ones more narrow than in *Z. Mays*. The pistillate spikelets are in pairs at the joints of the rhachis, the internodes of which are more or less strongly margined and cupulate, and finally become hard and shining. The glumes are very broad, strongly concave and enfolding each other, much more so than in the flowers of *Z. Mays* that I have examined, and than they are represented in the figures of Nees and Doell. The lower glume becomes very hard and rigid, excepting its margin, and firmly embraces the lower part of the kernel.

The ears upon the plants raised in the Botanic Garden were very variable, from scarcely two inches to four inches in length and three fourths of an inch broad, tapering slightly to an acutish apex, and with the kernels in four, eight, ten, and sometimes twelve, but most frequently in ten rows. A comparison of these shows clearly the structure of the ear. When there are only four rows, the ear is flattened and distichous, and the opposite pairs of rows are evidently the result of the pairs of spikelets regularly alternating upon the opposite sides of an extremely short-jointed and very flexuous rhachis. In the eight-rowed ear the rhachis is four-sided instead of two-sided, and in the ten-rowed it becomes five-sided. This latter case corresponds to the arrangement in the terminal raceme of the staminate inflorescence, where the spikelets are usually in five ranks. In the eight-rowed ear each joint bears two opposite pairs of spikelets, alternating with those of the joints immediately above and below, and in the twelve-rowed there are three pairs to each joint, alternating in the same way. The kernels are somewhat imbricated in the rows, and usually alternating, owing to one of the spikelets in each pair being slightly pedicellate. They are small, ovate, somewhat flattened dorsally and pointed, the lower part constricted by the closely embracing glume. In structure they are hard and corneous, with a central starchy layer extending from the base nearly to the apex. The ripened ear breaks readily at any point, so that the eight-rowed ear, for example, may be separated into its several joints, each bearing two opposite pairs of kernels. I would therefore characterize the new species as follows: —

Z. CANINA. Culms several from the same root, ascending, branched: staminate racemes often elongated and drooping; spikelets 2 to 4 (usually 3) at each node, one or more short-pedicelled: empty glumes 3–5-nerved, bicarinate: pistillate spikes sessile in the axils and terminal, the terminal staminate at the apex; ears small, 4–12-rowed, dividing more or less readily at the joints; kernels small (3 to 4 lines long), white, hard and smooth, ovate, acutish, constricted at base.

The location from which the specimens were obtained for Prof. Dugès is stated more definitely to be Moro Leon (otherwise Congregacion), near Uriangato, about four Mexican leagues north of Lake Cuitzeo. It is therefore near the boundary line between the States of Guanajuato and Michoacan. The natives of the district are said by Prof. Dugès to believe the *maïs de coyote* to be the source of the cultivated varieties of maize, notwithstanding the recognized differences between them. The kinds of corn in cultivation about Guanajuato are described by Prof. Dugès as the *maïs arribeño*, with hard and shining kernels; *maïs commun*, softer and less shining, either yellow, black, or red; *maïs molonco*, resembling the last, but with smaller kernels, growing in the "bad lands," and the difference probably due to the poverty of the soil; and a popcorn, *maïs rosero*. All of these are affirmed to be very unlike the *maïs de coyote*, which appears to be known only in a wild state.

As shown by Dr. Sturtevant in the Report of the N. Y. Agricultural Experiment Station for 1886, the varieties of corn cultivated generally by the Indians of Mexico all come into the group designated by him as "soft corns" ("*Zea* amylacea*"), in which the broad flattened kernels are composed wholly of starchy matter in addition to the embryo. A peculiar kind was found by Dr. Palmer at the Indian village of San Padro, Guadalajara, of which Dr. Sturtevant forms the distinct group of "starchy sweet corns" ("*Zea* amylea-saccharata*"), intermediate between the sweet and soft corns, having a wrinkled exterior and the summit of the kernel corneous. It is evident that so far as the grain is concerned these have little resemblance to the *maïs de coyote.*

4. *Notes upon a Collection of Plants from the Island of Ascension.*

During the visit of the U. S. Eclipse Expedition of 1889 to the island of Ascension, Mr. E. J. Loomis of the Nautical Almanac Bureau, Washington, made a collection of such plants as chanced to attract his attention. Though very small, it adds some species to the previously known flora of the locality, a full account of which is given by Mr. W. B. Hemsley in the botanical report of the voyage of the "Challenger." The vegetation of the island, as there stated, is restricted almost wholly to "Green Mountain," an elevation of nearly 3,000 feet altitude, which condenses the moisture of the southeast trades, and is consequently subject to frequent rains and fogs. At about three hundred feet below the summit the peak is encircled by a nearly level road, known as "Elliott's Pass," which generally follows the very irregular contour of the mountain, but is occasionally carried through a spur by means of a tunnel. When these tunnels are short, they are lined throughout, roof and sides, with the most delicate and beautiful ferns, as are also the longer tunnels so far as daylight extends. It was on this part of the mountain that much of the collection was made.

The entire phænogamous flora native to the island, as given by Mr. Hemsley, includes but twelve species, and ten of these are marked by him as only doubtfully indigenous. The two other species, *Hedyotis Adscensionis* and *Euphorbia origanoides*, are endemic. The cryptogamous flora is somewhat more extensive, the same authority giving a list of fourteen ferns (including a *Lycopodium*), thirty-five mosses and hepatics, and a dozen lichens.

The following is a list of the species of every kind collected by Mr. Loomis, of which those in italics are without doubt introduced plants. The species of ferns described as new have been submitted to Prof. Eaton and to Mr. J. G. Baker. The mosses were determined by Prof. C. R. Barnes, the single hepatic by Prof. L. M. Underwood, and the lichens by Prof. Farlow. It is to be regretted that the opportunity could not have been improved to make a larger and more complete collection of the plants of the island, for it is probable that a thorough search would increase considerably the number of indigenous species now known.

Argemone Mexicana, L. Abundant.

Senebiera didyma, Pers.

Oxalis corniculata, L.

RUBUS NANUS. Stems very short (1 or 2 inches high), from a woody caudex, erect, armed with numerous short recurved prickles, about 3-flowered at the summit: stipules narrow, acuminate, entire or sparsely toothed; petioles short, pubescent and prickly; leaves mostly simple and rounded, subcordate at base, unequally and subincisely serrate, somewhat 3-lobed or sometimes ternate, sparsely villous above, prickly on the veins beneath: calyx small (about 4 lines broad), the base prickly: carpels rather numerous, on a depressed receptacle, glabrous; styles short. — Described from a single specimen found near the entrance of a tunnel in Elliott's Pass. It appears to be a very distinct and peculiar species of a genus not otherwise represented in the flora of the islands of the South Atlantic.

Bidens pilosa, L.

Lactuca Scariola, L. (?) Foliage only.

EUPHORBIA ORIGANOIDES, L.

Commelina nudiflora, L.

CYPERUS UMBELLATUS, Benth. Foliage only.

LYCOPODIUM CERNUUM, L.

PTERIS INCISA, Thunb.

PTERIS FLABELLATA, Thunb., var. ASCENSIONIS, Hook. & Bak.

ASPLENIUM ASCENSIONIS. Stipes slender, tufted, an inch long or less, naked, dull brownish green; frond 3 to 6 inches long, often rooting at the apex, 6 to 10 lines broad, the rhachis channelled above and narrowly winged; pinnæ about 20 (15 to 25) on each side, very irregular in shape (nearly as in *A. fragile*), in the middle of the frond somewhat quadrilateral and nearly twice longer than broad, often more or less deeply lobed at base on the upper side, obtuse, irregularly and obtusely few-toothed or the lower margin entire, the lowermost usually round-deltoid, nearly equilateral and often lobed both sides, the uppermost becoming cuneate-obovate: sori linear-oblong, oblique, 1 to 6 on each side. — This adds another species to the closely allied *A. viride* group, intermediate between *A. fragile* and *A. vagans*. It is probably the same as the *A. dentatum* reported by Bory as collected on the island by D'Urville. Mr. Baker informs me that he also finds a specimen in Herb. Kew, among their *A. fragile*, which was given by "Don" (probably George, the younger, and collected by him on his trip to Sierra Leone) to Lindley in 1831.

NEPHRODIUM MOLLE, Desv. Specimens very variable and mostly much reduced.

NEPHRODIUM (?) VISCIDUM. More or less densely glandular-fibrillose throughout; stipes from a slender creeping rhizome, brown, about an inch long, bearing a lanceolate acuminate pinnate frond 3 inches long; pinnæ (except the upper ones) cleft nearly or quite to the midvein, the thin broadly oblong segments (1 to 2 lines long) obtuse, more or less crenate-serrate, glandular-villous beneath. — A single specimen, not in fruit, and the genus consequently indeterminate. Though strongly marked by its glandular-fibrillose character, it is not recognized by either Mr. Baker or Prof. Eaton. The former thinks it a starved *Nephrodium*, but "it cannot be *N. Ascensionis*," the only species excepting the last that is known from the island.

GYMNOGRAMME ASCENSIONIS, Hook.

CAMPYLOPUS INTROFLEXUS, Brid.

RHACOPILUM GRACILE, Mitt.

DICRANELLA —— ?

LEJEUNIA PTEROTA, Taylor.

THELOSCHISTES CHRYSOPHTHALMA, Norm., var. FLAVICANS, Wallr.

PARMELIA SAXATILIS, Ach.?

XII.

CONTRIBUTION FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

DESCRIPTIONS OF NEW PLANTS, CHIEFLY *GAMOPETALÆ*, COLLECTED IN MEXICO BY C. G. PRINGLE IN 1889 AND 1890.*

By B. L. Robinson.

Presented by Sereno Watson, April 8, 1891.

Xylosma Pringlei. Monœcious, glabrous, armed at the nodes with simple acicular spines 3 to 5 lines in length: leaves small, fascicled in the axils of the spines, coriaceous, elliptical, obtuse, attenuate to a subsessile base, serrulate, veiny, shining above, pale beneath, 9 to 16 lines long by half as broad; the edges more or less revolute and the teeth incurved: flowers fasciculately grouped, 3 to 6 together, with no common peduncle; pedicels slender, 3 or 4 lines long: sepals 4, ovate, acutish, scarcely exceeding half a line in length, glabrous or puberulent on the outer surface, ciliate, minutely pubescent within: stamens 12 to 18, twice as long as the sepals: style 2–3-cleft, and the ovate ovary incompletely 2–3-celled; fruit not seen. — In the Sierra Madre near Monterey, August, 1889 (n. 2784). This is perhaps the same as Dr. Palmer's n. 1062 (collected between San Luis Potosi and Tampico), which differs principally in its ovate leaves and verrucose stem.

Desmodium Jaliscanum, Watson, var. (?) obtusum. Stem 5 to 10 feet high: leaves elliptic, oblong, or even slightly obovate, very obtuse, apiculate: calyx-teeth ovate, obtusish, the upper one retuse; pods appressed-pubescent, very numerous in dense simple or branched racemes. — Rocky slopes, Tamasopo Cañon, San Luis Potosi; October, 1890 (n. 3290).

Pimpinella Mexicana. Glabrous: root more or less thickened; stem 4 feet high, with scanty foliage, paniculately branched above: the radical and lower cauline leaves very long-petioled, ternate; leaf-

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* Of the plants here described the last three only were sent from California and Washington by other collectors.

lets deeply 2–3-parted, the segments ovate or lanceolate, acuminate, more or less narrowed at base, 1 to 1½ inches long, 10 lines or less in breadth, green above, pale beneath, serrate, the margins of the teeth being slightly thickened and cartilaginous; upper leaves scattered in the diffusely branched inflorescence, pinnately or ternately parted with long linear toothed or serrate segments; the highest leaves reduced to filiform bracts; involucres and involucels none: umbels numerous, with few (2 to 6) often unequal rays 6 to 9 lines in length: umbellets about 12-flowered, only 2 or 3 flowers in each being fertile: corolla white (?) or in the sterile flowers not infrequently purple: fruit a line long, the ribs not very prominent; stylopodium depressed, the margin crenate; oil-tubes numerous; inner surface of the seed plane or very shallowly concave. — Hills of Patzcuaro, Michoacan; November, 1890 (n. 3331).

EUPATORIUM ESPINOSARUM, Gray, var. SUBINTEGRIFOLIUM. Leaves ovate, acuminate, subentire, very glutinous on both sides: scales of the involucre a little longer and more acute than in the typical form, being in these respects more as in var. *ambiguum*, Gray. — Shaded ledges of lime-rock, San José Pass, San Luis Potosi; October, 1890 (n. 3311).

GYMNOLOMIA DECUMBENS. Stems several from a ligneous base, decumbent, simple or branched from near the root, smoothish below, roughened above with very short appressed hairs: lower leaves opposite, elliptical, acute, narrowed to a sessile base, subentire, thickish, rough-pubescent, green on both sides, 1½ inches long by half as broad; the upper similar but narrower, alternate, sparse: heads terminal, solitary or 2 or 3 together; involucre ½ inch in diameter; outer scales ovate, acuminate, very rough, the inner larger, smoother, obtusish; chaff oblanceolate, acuminate; rays 12 to 15, narrow, over half an inch in length, yellow; achenes (immature) smooth, angled, and with no trace of teeth or awns. — Rocky hills, Tultenango, State of Mexico; September, 1890 (n. 3263). This species resembles *G. rudis*, Gray, but differs in its decumbent habit, smaller and more entire leaves, smaller heads, ovate not oblong involucral scales, and longer narrower rays. From *G. multiflora*, Nutt., it differs in the ligneous clearly perennial base, as well as in the involucre, etc.

OTOPAPPUS ALTERNIFOLIUS. Stem 3 to 6 feet high, striate, smoothish or slightly tomentulose: leaves alternate, ovate-lanceolate, acuminate at both ends, subsessile, with a short roughish pubescence above, white-tomentose beneath: heads in an open corymb, about 15, half an inch or more in diameter; scales of the involucre in several rows, narrowly oblong or lanceolate, some rounded at the apex, others acute: rays 12 to 25, little exceeding the disk; pappus of two very unequal awns, the inner more than half as long as the achene, the outer much shorter; achenes smooth, with a single rib on each face, edges acute, the outer usually wingless, the inner with a narrow wing, which extends up upon the inner awn and there broadens into an auricular appendage. — Limestone hills, San José Pass, San Luis Potosi; October, 1890 (n. 3310). From its peculiar pappus with wing-appendages this plant must be referred to the genus *Otopappus* as extended by Hemsley (Biol. Cent. Am. Bot. 2. 191), and placed near *O. epaleaceus*, Hemsl. The whole habit of the plant with its alternate leaves is that of a *Verbesina*, and it seems thus to connect the two genera, especially since there are several species of *Verbesina*, as *V. Humboldtii*, Spreng., and *V. perymenoides*, Schultz Bip., in which the achenes are more strongly winged on one side than on the other.

SENECIO GUADALAJARENSIS. Herbaceous; stem erect, leafy, sulcate-striate, smooth: leaves elongated lanceolate, 6 to 8 inches long, 9 to 15 lines broad, acute, narrowed at base to a very short naked petiole, pinnately veined, callous-denticulate and minutely ciliate, coriaceous, glabrous on both sides except the veins beneath, the upper surface green, covered with lighter-colored warty blotches (pathological?), the lower surface very glaucous: corymb ample, with rather numerous medium-sized heads; scales of the involucre about 10, strongly carinate, acutish, 4 lines long: rays about 5, rounded at the apex; teeth of the disk-corollas exceeding the short campanulate throat and half the length of the slender tube proper: achenes ribbed, puberulent. — Rich slopes of barranca near Guadalajara, Jalisco; September, 1890 (n. 3280).

LAURENTIA OVATIFOLIA. Annual, 6 to 12 inches high, puberulent; stem slender, flexuous, angled, subsimple or branched above: leaves petiolate, ovate, acute, abrupt or subcordate at base, finely and regularly serrate, about an inch long, two thirds as broad, the lowest smaller, rounder, obtuse, the upper lanceolate; petioles 3 to 5 lines long; pedicels filiform, curving upward, 9 to 12 lines long, two to four times longer than the linear-filiform bracts: flowers small, racemose; calyx-tube hardly any, the lobes linear, acute, not quite equalling the corolla-tube; corolla 2 lines long, the nearly white tube split half-way to the base behind; limb blue, with very dissimilar lobes, the three lower obovate, somewhat united to form a spreading lip, the two upper erect, contracted to narrow points: stamens inserted near the middle of the tube, the two smaller anthers penicillate: capsule ovate-oblong or elliptic in outline, papery, almost entirely superior, 2-valved at the apex. — Shaded banks near Guadalajara; September, 1889 (n. 2985); also near Cardenas, San Luis Potosi, 1890 (n. 3302). This plant, which was distributed under the name of *Laurentia Michoacana*, var. *ovatifolia*, appears on further examination to be distinct from n. 3337, of which it was at first regarded as a variety. It has the habit of a *Lobelia*, but the corolla is split behind only part way to the base. While in the limb of the corolla and the insertion of the stamens it agrees rather closely with *Palmerella*, the corolla-tube is short, as in *Laurentia*. The plant thus furnishes additional evidence that Schönland is right in uniting the two genera.

Mr. Pringle's n. 3337, the plant which was distributed as *Laurentia Michoacana*, Robinson, is without doubt closely related to the species just described, but is distinguished by its sessile leaves of considerably different form and toothing. It appears to be identical with Parry & Palmer's n. 557, which Hemsley refers to *Lobelia micrantha*, HBK., and with Mr. J. Donnell Smith's n. 22, the *Lobelia Türckheimii* of Vatke (unedited?). The corolla in all these plants, however, is cleft only from one third to half-way to the base, a character which should certainly exclude them from *Lobelia*, as at present defined by Bentham & Hooker, Baillon, Schönland, and others. While the specimens in question agree in most points with *Laurentia ramosissima*, Benth. & Hook. (*Lobelia ramosissima*, Mart. & Gal.), they are distinguished by their much smaller flowers. Unfortunately, however, Martens and Galeotti have characterized, under the name of *Lobelia parviflora*, a plant which also appears from their rather unsatisfactory description to differ from their *Lobelia ramosissima* chiefly in the same respect, namely the shorter corolla. This being the case, it seems best that all three of the numbers just cited should be for the present doubtfully referred to *Lobelia parviflora*, Mart. & Gal., since it is highly probable that the type of this species will be found on investigation to be a *Laurentia*, just as the *Lobelia ramosissima* of the same authors has already proved.

LOBELIA NOVELLA. Stem a foot high, branching, with a few rather large leaves near the base, almost naked above: leaves petiolate, broadly ovate, acute or obtusish, rounded or subcordate at base, undulate and finely mucronate-denticulate, hispid on both sides, scarcely paler beneath, 2½ to 3 inches long, 2 inches in breadth; upper leaves few, much smaller, sharply and doubly denticulate; racemes long, secund; bractlets minute, scarcely exceeding a line in length; pedicels 6 to 9 lines long: calyx-tube turbinate, in fruit equalling or surpassing the narrowly linear obtuse lobes; corolla blue and white, the lobes of the lower lip obovate-spatulate, longer than the very narrow upper lobes: capsule half-inferior. — Cool ledges and gravelly banks, Tamasopo Cañon, San Luis Potosi; October, 1890 (n. 3288). Resembles *L. Sartorii*, Vatke (ex char.), but is distinguished by the elongated racemes, and by the size, shape, and indentation of the leaves.

NEMACLADUS OPPOSITIFOLIUS. Stems a foot high, much branched from near the ground; branches becoming erect from a decumbent base, usually simple, each bearing about six pairs of subopposite leaves, and then continued as a long naked racemose inflorescence: leaves petiolate, ovate, acuminate, rounded at base but inconspicuously decurrent upon the petioles and stem, sharply dentate, smooth, 9 to 15 lines long; petioles 2 or 3 lines in length; bracts minute, awl-shaped, scarcely a line in length, the bractlets subtending the calyx similar; pedicels not exceeding 2 lines long: calyx-tube short, rounded at base, the segments equal, awl-shaped, acute, a line long; corolla-tube not equalling the calyx-lobes, the lower lip consisting of two ovate spreading segments, much longer than the three upper lobes: stamineal column ascending against the upper lip of the corolla and then curved forward; anthers stellately divaricate around the stigma, not at all appendaged: mature capsule nearly equalling the calyx-lobes, two-valved at the apex. — Dry calcareous bluffs near Cardenas, San Luis Potosi; October, 1890 (n. 3300). This plant, which is identical with Dr. Coulter's n. 30, differs greatly in habit from the known species of *Nemacladus*. It possesses, however, just the characters which distinguish this genus in such a marked manner; namely, the stellately divaricate anthers, and the division of the corolla into a three-lobed upper lip and a two-lobed lower lip. The subopposite leaves appear to be anomalous among the *Lobeliaceæ*.

SYMPLOCOS PRINGLEI. A small tree, 20 to 30 feet high; branchlets and petioles covered with a very short rufous tomentum: leaves elliptical, varying from obtusish to abruptly acuminate, cuneate at base, sharply and regularly serrulate, subcoriaceous, green and glabrous above, slightly paler beneath and pubescent especially along the midrib, 2½ to 4 inches long by 1½ broad; petioles 4 to 6 lines long: flowers usually aggregated by twos and threes, subsessile upon a scarcely distinguishable common peduncle, occasionally solitary: calyx silvery-sericeous; lobes ovate, rounded or more or less pointed at the apex; petals 5, broadly spatulate, coherent for a third of their length, either smooth or very minutely pubescent on the outer surface: stamens obscurely 4–5-delphous, united high up, adnate to the corolla for half its length: lower part of the style as well as the apex of the ovary strongly hirsute; ovary 3-celled: fruit oblong, dark-colored, with slight puberulence, tipped with the hardened calyx-teeth. — Hills of Patzcuaro, Michoacan; November, 1890 (n. 3345). Resembles in many respects *S. prionophylla*, Hemsl. (ex char.), but has leaves not at all ovate, and the petals nearly smooth and united with each other and with the stamens for about half their length. In the species just mentioned they are described as nearly or quite free.

GONOLOBUS PARVIFLORUS, Gray, var. BREVICORONATUS. Corolla erect, instead of being reflexed as in the type; the outer crown of five short rather thick truncate scales, which are not at all produced into lobes at the edges; the inner crown of five horns as in the typical form. — Laredo, Texas; July, 1889 (n. 3029).

BUDDLEIA CHAPALANA. Suffruticose; branches with a smooth yellowish bark; branchlets woolly: leaves ovate or ovate-oblong, 1½ to 2½ inches long, an inch broad, appearing more or less rhombic in outline from being contracted at base into a broadly winged petiole, auriculate-perfoliate, acute, rather coarsely and bluntly toothed, woolly on both sides when young, becoming nearly smooth at maturity and retaining only a slight mealiness; floral leaves much smaller, lanceolate, scarcely perfoliate: flowers in globular heads; the heads half an inch in diameter and borne in pairs on axillary peduncles about 4 lines long; corolla 1½ lines in diameter, short, not or scarcely exceeding the woolly calyx. — On dry cliffs in the mountains near Lake Chapala, Jalisco; December, 1889 (n. 2972).

CORDIA PRINGLEI. A shrub 10 to 15 feet high, belonging to the section *Dasycephalæ*; branchlets, peduncles and petioles stellate-tomentose: leaves ovate or ovate-oblong, more or less narrowed to an obtuse apex, often one-sided, all but the smallest abrupt or even subcordate at base, crenate-dentate with irregular teeth, green and finely stellate-pubescent above, lighter and tomentose beneath, 3 inches long, 1 or 2 inches broad; petioles 6 lines in length: heads globular, an inch in diameter on subterminal peduncles 1½ inches long; calyx narrowly campanulate, the tube white-pubescent, and the filiform teeth stellately ferruginous-pubescent, curled irregularly, mostly reflexed: corolla funnel-form, white, 5 lines broad, with obtuse lobes: stamens inserted near the summit of the pubescent throat. — Las Palmas, San Luis Potosi; June, 1890 (n. 3091). Differs from *C. ambigua*, Cham. & Schl., in its larger heads and the abrupt or subcordate bases of the leaves, as well as in the absence of the long spreading hairs on the petioles and peduncles. Mr. Pringle's plant much resembles a specimen from Nicaragua, collected by C. Wright (N. Pacif. Expl. Exped. 1853–56). The latter differs, however, in its larger flowers and more finely toothed leaves, which are more densely and roughly pubescent upon the upper surface.

HELIOTROPIUM PRINGLEI. A spreading annual, branching from the base, 2 to 5 inches high, silky-villous: leaves elliptic-lanceolate, acute at both ends, 4 to 6 lines long, 2 lines broad; petioles 1 or 2 lines long: flowers scattered along the leafy branches from near the base; calyx-lobes lance-linear, acuminate: corolla-tube 1 to 1½ lines long, the limb abruptly expanding, 2½ lines broad, with five acutish primary lobes, with which five short teeth alternate: fruit separable at maturity into four nutlets, minutely reticulate-roughened on the back but not hispid. — Santa Eulalia Mountains, Chihuahua, October, 1886 (n. 1160); also in thin soil of rocky hills, Las Canoas, San Luis Potosi, July, 1890 (n. 3207). This species resembles in habit *H. phyllostachyum*, Torr., but has flowers more than twice as large. It is distinguished from *H. limbatum*, Benth., under which name n. 1160 was distributed, by its broader leaves, very scattered flowers, more acute lobes of calyx and corolla, rougher nutlets, and its more decidedly annual character. The inflorescence in *H. limbatum* is distinctly terminal and compact, and the root often clearly perennial.

OMPHALODES ACUMINATA. Stem weak, procumbent, diffusely branched, nearly smooth, 18 inches long or more, leafy throughout: leaves deltoid, attenuate-acuminate, entire, 2 inches long, 15 lines in breadth, cordate with rounded lobes and broad sinus, membranaceous, nearly smooth above, puberulent with very short hairs beneath; the upper leaves smaller, lanceolate, subcordate or rounded at base: petioles 1 to 1½ inches long: peduncles lateral, scattered, very slender, flexuous-spreading, 9 to 12 lines in length: calyx-lobes oblong, acute; corolla 4 or 5 lines broad, rose-color, with short tube and rounded spreading segments; scales very prominent, nearly globular, minutely papillose: nutlets orbicular, only one in each flower ripening, 1½ lines in diameter at maturity, flat, horizontal over the gynobase, the wing reflexed, about 30-toothed. — In the Sierra Madre, near Monterey; June, 1888 (n. 2220). Resembles *O. cardiophylla*, Gray, but is smoother throughout and has much longer stems of more straggling habit, the leaves twice as large, of more delicate texture, and much more attenuate at the apex. In that species, moreover, two to four nutlets mature and the wing-borders have but half as many teeth.

IPOMOEA LEONENSIS. Root tuberous, an inch thick: stem twining, striate-angulate, minutely roughened: leaves deeply palmately 5-lobed, cordate or subcordate, 3 to 5 inches broad, punctate above and with a soft deciduous tomentum beneath, the lobes lanceolate, rounded at the apex and inconspicuously mucronate, or in young leaves sometimes acutish, the two outer lobes of the larger leaves each appendaged at base with a large blunt auricle; petioles an inch long or more, roughened especially near the base by numerous small tuberculate glands: peduncles 2 inches long, 1-flowered, puberulent; bractlets minute or obsolete; pedicels half an inch long: sepals ovate, with rounded apex, 4 lines long, canescent with very short appressed silvery hairs; corolla nearly 3 inches long, twice the length of the stamens, purple. — Calcareous ledges near Monterey; June, 1889 (n. 2840). Allied to *P. digitata*, L., but differing in its 1-flowered peduncles and glandular petioles, as well as in the shape and pubescence of the leaves. The flowers are also larger and the throat relatively narrower.

BASSOVIA MEXICANA. A shrub, 5 to 15 feet high; branches unequally dichotomous, slightly striate-angled and minutely verrucose: leaves membranaceous, geminate, ovate, acuminate, the larger 1½ to 2 inches long, ¾ to 1 inch broad, the smaller half as large, all abrupt at base or slightly decurrent on one side upon the slender petiole, green on both sides, slightly scabrous above, sparsely pubescent on the veins beneath: inflorescence umbelliform, sessile, axillary; pedicels 2 to 6, 1-flowered, 4 to 5 lines long, striate, slightly thickened upward: calyx spreading, shallow cup-shaped, strictly truncate, persistent; corolla 3 to 3½ lines in length, divided to the middle or even more deeply; tube short, slender; limb campanulate, of 4 or 5 lanceolate acuminate segments, puberulent upon the outside; stamens exserted, the filaments at maturity exceeding the anthers; throat of the corolla and base of the filaments bearded: fruit the size of a pea, red (turning black?), many-seeded; seeds a little over half a line in diameter, compressed, roughened with pits. — Tamasopo Cañon, San Luis Potosi; June, 1890 (n. 3071). Resembles some species of the genus *Brachistus* in its truncate calyx, but has the deeply cleft valvate corolla of *Bassovia*, and shows close affinity to *B. macrophylla*, Benth. & Hook. (*Witheringia macrophylla*, auct.), from which it differs principally in its ligneous stem, much smaller leaves, fewer-flowered fascicles, and more persistent calyx. The distinctions between *Bassovia* and *Brachistus* are not at all satisfactory, and considering the intermediate character of this new species it seems best to refer it to the older genus.

WITHANIA (?) MELANOCYSTIS. A shrub, 5 to 8 feet high, minutely pubescent on the leaves and younger parts; branches gray, striate: leaves single or geminate, lanceolate to ovate-lanceolate, acute, entire

15 lines long by 6 wide, narrowed at the base into a petiole 3 to 4 lines in length: flowers 2 to 4 at each node, usually but one of each group fruiting; common peduncle none; pedicels slender, 3 lines long: calyx-teeth 5, at anthesis ovate, one third as long as the tube; fruiting calyx much enlarged, bladder-like, neither angled nor conspicuously veined, becoming black, 9 lines in diameter, with throat contracted and teeth relatively short; corolla campanulate, 5 lines long, with a more or less spreading limb of five ovate acutish segments equalling the tube, pale yellow with conspicuous dark spots in the puberulent throat; filaments inserted in the middle of the short tube, half the length of the oblong anthers: berry globular, red, much smaller than the enclosing calyx; seeds roughened, compressed, yellow. — Tamasopo Cañon, San Luis Potosi; June to October, 1890 (n. 3285). A plant of puzzling affinities, possessing the habit of a *Physalis*, but having a woody stem, clustered flowers, calyx without conspicuous angles or veins, and anthers much exceeding the filaments. Some of the characters resemble those of *Athenæa;* in that genus, however, the fruiting calyx is much more deeply divided.

HERPESTIS AURICULATA. Roots fibrous; stem erect, smooth, sharply 4-angled, much branched above, a foot high; branches mostly simple: leaves lanceolate, acute, serrulate, sessile with an auriculate-clasping base, punctate, 8 to 10 lines long, 3 lines broad: floral leaves gradually reduced to linear bracts 2 to 3 lines long: flowers small, axillary, mostly in pairs, opposite at each node; pedicels filiform, 3 lines long; divisions of the calyx acuminate, a line long, becoming 1½ lines long in fruit, very unequal in breadth, three of them ovate, the inner two rather narrowly lanceolate, none of them at all oblong; corolla purplish, 3 lines long, slightly bearded within near the summit of the tube; rudimentary stamen present, very small, subulate: capsule depressed-ovoid, subglobose, not exceeding the calyx, 2-valved. — Wet places near Guadalajara; November, 1889 (n. 2937).

GERARDIA PUNCTATA. Stem puberulent, much branched: leaves small, numerous, opposite or appearing fascicled, linear, entire, acute, smooth, 7 to 10 lines long, a line or less in breadth; bracts similar: flowers rather numerous, opposite in long subspicate racemes; pedicels 1 to 2 lines long: calyx smooth, 10-nerved, often punctate with small purple dots, the five teeth lanceolate, acuminate, exceeding the tube, the intermediate nerves terminating at each sinus in a minute glandular prominence; corolla purple, tubular-campanulate, an inch long, the lobes a fourth as long as the tube; stamens conspicuously didynamous, the upper pair being much shorter and having considerably smaller anthers than the lower; filaments glabrous; anthers hirsute, mucronate at the base of each cell: style puberulent; capsule ovate, acuminate, equalling the calyx-lobes; seeds oblong, light brown, the external seed-coat loose, cellular, and iridescent. — Hills of Zacatecas: October, 1888 (n. 2183).

CASTILLEIA MACROSTIGMA. Perennial, 8 inches to a foot high, nearly smooth or more or less hispid with weak spreading hairs: leaves small, rather numerous especially at the base, linear, acute, entire, subamplexicaul, 1–3-nerved, 9 to 15 lines long, seldom exceeding a line in breadth; floral leaves broader and shorter, lanceolate or narrowly ovate, angled or sparingly toothed toward the apex, often yellow-tipped: flowers closely sessile in a short spike, slender, 8 to 12 lines long, surpassing the bracts; calyx light yellow, equally cleft before and behind, the lobes emarginate or two-toothed; corolla a third longer than the calyx, yellow, the lower teeth linear, acuminate, erect: stigmas conspicuously exserted, thickish, sometimes more than a line long, recurved. — Grassy slopes, Flor de Maria, Mexico; July, 1890 (n. 3194). This appears to be the same as Mr. Pringle's n. 1545 from Chihuahua, which was distributed under the provisional and unedited name of *C. lithospermoides*, HBK., var. (?) *flava*, Watson. Specimens of this number differ from 3194 chiefly in being more hispid and in having the stigmas less prominently exserted, which differences may be in part due to the less advanced stage of development. Both plants differ from *C. lithospermoides* in the size and color of the corolla, in the deeply cleft conspicuously exserted stigma, and also in the shorter relatively thicker and more coarsely reticulated seeds.

RUELLIA BOURGÆI, Hemsley. The mature capsules of this species, which were wanting in the type specimens and could not therefore be described, are excellently shown in Mr. Pringle's n. 2951 (barranca near Guadalajara, September, 1889). They are rigid, lanceolate, acutish, cuspidate, glabrous, 2 to 2¼ inches long and ½ inch broad, the valves with a conspicuous median furrow; hooks ascending, bifid; seeds orbicular, nearly 3 lines in diameter.

JUSTICIA PRINGLEI. Herbaceous, 2 feet high, hirsute with spreading white hairs: leaves ovate, acuminate, entire, petiolate, 1½ to 2½ inches long, half as wide; the lowest smaller, orbicular, obtuse: flowers small, distant, borne in a spreading panicle; lower bracts foliar, ovate, the upper much smaller, lanceolate; bractlets minute, awl-shaped, half the length of the calyx; calyx-teeth 4, narrowly linear, attenuate, 2½ to 3 lines long; corolla 4 to 5 lines long, pale rose-color, the limb nearly equalling the tube, the upper lip narrowed to a retuse summit, the lower lip rounded: anther-cells nearly equal in size, the upper not ciliate, minutely mucronate at the base, the lower with a conspicuous spur: capsule 5 lines long, soft-pubescent, 4-seeded; seeds compressed, very hairy especially at the edge. — On hills near Guadalajara; October, 1889 (n. 2967). This species seems anomalous among the New World members of the genus. It resembles more nearly the species of the § *Rhaphidospora* of the Old World, which have a diffuse inflorescence and echinate-hispid seeds. It differs from § *Sarotheca* chiefly in lacking the ciliation of the anthers.

CITHAREXYLUM BERLANDIERI. Ten to fifteen feet high; branches gray, striate; branchlets pubescent, striate, acutely 4-angled but soon becoming round: leaves ovate or rhombic, varying in the same individual from acute to retuse at the apex, shortly cuneate at base, membranaceous, puberulent above, soft-pubescent beneath, 1 to 1¾ inches long, 9 lines broad, entire, or some with a few blunt teeth near the apex: inflorescence terminal, subspicate, more or less flexuous, 1 to 2 inches long, becoming more rigid in fruit; pedicels half a line long, with minute filiform bractlets of the same length: calyx turbinate, 2 lines long, striate, pubescent, the five subequal teeth erect, very short and blunt: corolla-tube just equalling the calyx, pubescent within, the spreading limb of five rounded lobes, puberulent on both sides: fertile stamens four, filaments hairy; the fifth stamen present as an antherless rudiment: drupes dark brown, as large as peas, crowded in the spikes. — Rocky hills, Las Canoas, San Luis Potosi; July, 1890 (n. 3222). Apparently identical with n. 3182 of Berlandier, collected near Matamoras, May, 1832. This specimen of Berlandier's was doubtfully referred by Dr. Gray to *C. villosum*, Jacq., and has formed the sole evidence that this species occurs in Mexico. In the light of Mr. Pringle's better material, however, it is clear that the Mexican plant is quite distinct from the species just mentioned.

SCUTELLARIA HISPIDULA. Perennial with ligneous base: stems numerous, mostly simple, hispidulous, a span high, often dark purple as well as the floral leaves and calyx: leaves small, ovate or ovate-elliptic, subglabrous or very minutely hispid but not at all cinereous-pubescent, 4 to 5 lines long (about half the length of the internodes), 2 to 3 lines broad, all except the very lowest abrupt at the base and sessile: flowers numerous, of medium size, with short pedicels; calyx strongly accrescent, hispid with short white hairs: corolla blue, white in the throat, soft-pubescent on the outside, 5 to 7 lines long, the upper lip but slightly cucullate: upper stamens often exserted. — Meadows, Flor de Maria, Mexico; August, 1890 (n. 3233). A plant with the habit of *S. Drummondii*, Benth., and *S. Wrightii*, Gray, but distinguished from the former by its ligneous base and clearly perennial nature, and from the latter by the form of the leaves, character of the pubescence, smaller blue flowers, and less cucullate upper lip. While it may ultimately prove to be a variety of *S. Wrightii*, such a disposition of it in the absence of connecting forms and with the difference of geographic occurrence would at present be unwarranted.

MIMULUS CONGDONII. Very small, at flowering subacaulescent; stems glandular-pubescent, becoming in fruit 1 to 4 inches high, much branched near the base; branches simple: leaves ovate or lanceolate, obtuse, entire, dark purple beneath, ½ an inch long, narrowed at base to ciliate petioles of nearly equal length; peduncles in fruit 1½ to 2 lines long, often reflexed: flowers very small; calyx-tube very slender, prismatic, glandular-puberulent, moderately gibbous at base, becoming strongly so in fruit, ending obliquely in short teeth, the upper tooth the longest; corolla rose-purple, the slender tube 4 to 6 lines in length, with little or no distinctly enlarged throat, the subregular abruptly spreading limb 1½ to 2 lines in diameter; stamens strongly didynamous, the upper pair much shorter and occasionally with abortive anthers: style puberulent above; capsule cartilaginous, very gibbous, laterally compressed, narrowed from a moderately broad base, acute, deeply furrowed on the sides; seeds minute, acute at each end. — Collected by Mr. J. W. Congdon, in Mariposa County, California, at Zimmerman's Ranch, in March, 1887, in April, 1888 (flowers and fruit), and in May, 1888 (fruit); also at Stockton Creek, March, 1889 (flowers); and at Agua Fria (fruit). The diminutive size and nearly acaulescent character of flowering specimens of this plant made it at first appear probable that it represented merely a dwarfed, early-spring form of one of the larger-flowered species. The constant characters of Mr. Congdon's specimens, however, collected as they were at different dates and localities, and representing very different stages of development, prove it a normal form and a distinct species. While the vegetative habit is much like that of *M. Kelloggii*, Curran, it is distinguished from that species by its much shorter corolla-tube and smaller limb, as well as by its acute and not at all oblong capsules. From *M. pulchellus*, Greene, it differs in its smaller rose-purple corolla without the yellow lip, in its much shorter calyx-teeth, and in other ways. In its short corolla-tube and very gibbous capsule it resembles *M. latifolius*, Gray, but differs in its smaller size, in its habit of branching from the base, (the stem of *M. latifolius* although branching above is simple below,) in its very slender calyx-tube, longer and usually reflexed peduncles, and relatively slender and more acute capsules. Like *M. latifolius*, this species is somewhat intermediate between §§ *Œnoe* and *Eunanus*.

Mimulus gracilipes. A delicate annual. 3 to 5 inches high; stem usually simple, glandular-puberulent under a lens: leaves about four pairs, very small, seldom exceeding 4 lines in length, sessile, lanceolate, obtusish or scarcely acute, entire or minutely denticulate. the roundish cotyledonary (?) leaves persisting at base: peduncles springing by pairs from each node, an inch long, filiform, spreading horizontally and gracefully curved upward: calyx oblong-campanulate, a little over 2 lines in length, a line in diameter, the equal teeth slightly spreading, obtuse, strongly ciliate; corolla rose-purple with yellow markings in the throat, the tube not quite twice the length of the calyx; limb spreading, 3 or 4 lines in diameter, strongly bilabiate, the upper lip much shorter than the ample 3-lobed lower one: capsule symmetrical, of delicate texture, elliptical in outline, 2 lines in length, included in the scarcely inflated calyx; seeds obtuse. apiculate at each end. — Collected by Mr. J. W. Congdon, at Mormon Bar, Mariposa County, April, 1889. Near *M. rubellus*, Gray, and *M. deflexus*, Watson, but differing from the former in its simple stem, much larger corolla, and longer peduncles; from the latter in the color of its corolla: and from both these and various other related species in its ciliate calyx.

Aster Engelmanni, Gray, var. (?) paucicapitatus. Slender; stem weak and flexuous: leaves numerous, oblong-elliptic. obtusish, apiculate, puberulent above and with scanty traces of tomentum beneath, 10 to 15 lines long, a fourth as broad: heads solitary. terminal, or sometimes 3 to 5; scales of the involucre more equal and less closely imbricated than in the typical form or other varieties; rays white or pink. — Collected by Mr. C. V. Piper in the Olympic Mountains, Washington, September, 1890. This is a very puzzling form and perhaps a distinct species. If, however. Dr. Gray was right in classing *A. ledophyllus*, Gray, and *A. Engelmanni*, var. *glaucescens*, as varieties of the same species, Mr. Piper's plants, which are in some regards intermediate between these varieties, should probably also be included in *A. Engelmanni*.

In closing, the writer wishes to express his warmest thanks to Dr. Sereno Watson for his kind and ready aid in many points of difficult classification and perplexing nomenclature.

XIII.

CONCERNING THE LIFE-HISTORY OF *SACCORHIZA DERMATODEA*, (DE LA PYL.) J. AG.

By William Albert Setchell.

Presented by W. G. Farlow, June 10, 1891.

We owe our first knowledge of this interesting species to Baron de la Pylaie, who discovered it in 1816, on his first visit to Newfoundland and the neighboring islands of St. Pierre and Miquelon. He deposited specimens of this plant with the Museum of Paris in 1817, and gave to it the name of *Laminaire en forme de cuir*, or *Laminaria dermatodea*. In his second voyage to Newfoundland, in 1819, De la Pylaie extended his observation on this species. In 1824 he published the name given to the herbarium specimens, as well as a few remarks on the affinities of the species, in the "Annales des Sciences Naturelles." But it was not until 1829, however, that he gave any detailed account of its form and structure. In that year he published the first part of the "Flore de Terre Neuve," a work which was to include descriptions of all the plants collected by him in the "New World." This part, however, was the only one ever published, and that lacks the plates intended to accompany it.

The description both of the external form and the internal structure published in the "Flore de Terre Neuve" is very full. De la Pylaie considered that it replaced on the shores of Newfoundland the *Laminaria bulbosa* of Europe, whose near relative he rightly judged it to be. The name was suggested by the thickness and leathery consistency of the adult plant.

The plant thus discovered and described has since been found in several other places, and a number of references have been made to it. A list of as many as have come under the notice of the writer is appended to this paper.

Distribution. — The range of *Saccorhiza dermatodea* seems to be circumpolar. It is found at Vancouver's Island, on the western coast of North America,* and along the shore of Southwestern Kam-

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* Harvey, Proc. Linn. Soc., Vol. VI. p. 166, 1862.

tschatka.[*] Kjellman also credits it to the North Pacific.[†] It is, indeed, unknown either in the American Arctic Sea[‡] or in the Siberian Sea; but the former has never been explored to any extent, and although the latter has been more thoroughly searched, the physical conditions over the greater portion of it are unfavorable to the growth of any algæ.[§] The species reappears in the Murman Sea,[‖] extends into the White Sea,[¶] and thence along the northern coasts of Norway.[**] In the Greenland Sea it occurs at Spitzbergen,[††] and at "Beeren Eiland."[‡‡] It is found in Baffin's Bay on the western coast of Greenland,[§§] and extends down along the eastern coast of North America nearly to Cape Cod.[‖‖]

From the scanty references to the occurrence of *Saccorhiza dermatodea* in the North Pacific, one might infer that it is very scarce there. The locality in the Arctic Ocean where it is most abundant is, according to Kjellman, the northern coast of Norway; but even there, he says, "it does not occur in any such numbers as are comparable in any way with other *Laminariaceæ*." On page 96 of his "New England Algæ," Farlow has called attention to the fact that this species is of much rarer occurrence on the New England coast than almost any other species of the same family: and that, while rare at its southern limit in the region of Boston, Mass., it becomes more abundant on the coast of Maine. My own experience in collecting on the New England coast fully confirms this. It has never been found growing south of Nahant, Mass., where it is ordinarily rather rare. Farther north at Portland and Mount Desert Island, Maine, it is more plentiful, while at Eastport, Maine, it is said to be fairly abundant.

Habitat. — Eaton[¶¶] records that a specimen was brought up by the dredge through twenty-five fathoms of water off Campobello Island,

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[*] Rupr., Tange Och., pp. 352 and 409, 1847.

[†] Arct. Alg., p. 38, 1883.

[‡] Cf. Kjellman, *loc. cit.*, pp. 4 and 5, for the divisions of the Arctic Sea.

[§] Kjellm., *loc. cit.*, p. 26.

[‖] Kjellm., Alg. Murm., p. 36, 1877.

[¶] *L. Bærii*, Post. & Rupr., Ill. Alg., p. ii, 1840 (*fide* Areschoug).

[**] Aresch., Obs. Phyc., Part III. p. 11, 1875. Kjellm., Arct. Alg., p. 225.

[††] J. Ag., Spets. Alg. Till., p. 31, 1868. Kjellm., Arct. Alg., p. 225.

[‡‡] Kjellm., Arct. Alg., p. 225.

[§§] J. Ag., Grönl. Lam. och Fuc., p. 11, 1872.

[‖‖] De la Pyl., Ann. Sci. Nat., Ser. 1, Tom. IV. p. 179, 1824; Fl. Terre Neuve, p. 48, 1829. Farlow, N. E. Alg., p. 95, 1881.

[¶¶] Trans. Conn. Acad., Vol. II. p. 343, 1873.

near Eastport. Kjellman * says that "in the Arctic Sea proper the present species occurs in company with other *Laminariaceæ*, and is usually met with here at a depth of 2–10 fathoms on rocky or stony bottom"; but "on the coast of Norway," he says, "it does not belong to the proper formation of *Laminariaceæ*, but descends deeper than this, even to a depth of twenty fathoms. But it is most common here," he adds, "in shallow, rather exposed bays on gravelly bottom in 4–5 fathoms." Farlow states † that at Eastport it is found in deep pools, but that elsewhere it is an inhabitant of deep water. I have found it at Peak's Island, growing in shallow pools between tide marks, and down to eight or ten feet below low-water mark. I did not search for it at a greater depth. At Marblehead, Mass., it occurred in a very shallow pool at extreme low-water mark. At Nahant, in May and June, 1889, it grew in abundance just below low-water mark, and in pools between tides. But a number of specimens were found in two rather deep pools at the uppermost tide limit.

Season. — De la Pylaie mentions ‡ that numerous very young specimens were cast ashore about the end of October; and Kjellman states § that young individuals were common during the winter on the north coast of Spitzbergen, but that on the "coast of Norway younger and older specimens are of rather the same frequency during the summer months, in July and August." The season on the coast of New England seems to correspond with that of the coast of Norway. I have seen young specimens of *Saccorhiza dermatodea* only in late spring and summer. The first young specimens I found were growing at Nahant, just below low-water mark, June 23, 1888, and were only two or three in number. On April 24, 1889, on a visit to Nahant, I found the pools full of young *Laminarieæ* of small size, among which young specimens of the present species were tolerably abundant. These were of different lengths, and a number of specimens were collected. A careful search was made for the very earliest stages, but none were found. Some very small plants were obtained, but none of the very earliest. It may be present in large numbers in a given locality at one season, and almost entirely wanting during the next. In June, 1888, on the northeastern side of Peak's Island, hundreds of beautiful large plants were growing just a few feet below low-water mark; but in June, 1889, not a single plant was to be found in

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* Arct. Alg., p. 225.

† N. E. Alg., p. 96.

‡ Fl. Terre Neuve, p. 49.

§ *Loc. cit.*, p. 225.

the same locality, even after a very careful search. In June, 1888, only a very few plants were to be found in the tide-pools at Nahant, and those occurring in the very lowest; but in May and June, 1889, all the tide-pools were full of young plants, even the very uppermost. In the mass of kelps thrown ashore after storms are to be found comparatively few individuals of this species. They are usually more abundantly cast up in February and March than in the other months, and are for the most part old plants, which are often much mutilated.

Material. — The material on which the present paper is based was collected, for the greater part, by the writer on the shores of Maine and Massachusetts. During the year 1889 the tide-pools at Nahant, Mass., furnished an excellent place for observing this species in almost all of its stages. The first collections were made in the last week of April, and the locality was visited from time to time until June of the following year. Collections were also made at various times at Marblehead, Mass., and at Peak's Island, near Portland, Maine. From these various collections specimens of all ages were preserved in alcohol of about fifty per cent strength, and numerous notes and observations made from them while living. Consequently a number of interesting facts concerning the development have been revealed, and certain relationships more firmly established. In the following paper the morphology of the different periods in the life-history will be given first, and then the histological details of these same periods.

MORPHOLOGY.

Literature. — The first description of the plant is the one by De la Pylaie in the "Flore de Terre Neuve." He describes in full the morphology of the adult plant and that of several stages of development. He emphasizes one point about the origin of the permanent holdfast, which seems to have been entirely overlooked by later writers. Areschoug* was the next writer to add much to our stock of information. He gives a number of very valuable details concerning the size and form of some plants of different ages, and is the first to announce the discovery of this species in Northern Norway and to distribute specimens of it.† On the label of the specimen distributed he remarks, "cum speciminibus e Lapponica Rossica nomine *L. Bærii*, Post. & Rupr. acceptis melius quam cum specimini-

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* Obs. Phyc., Part. III. p. 11.

† Alg. Scand. Exss., No. 213, under the name of *Laminaria lorea*.

bus e Terra Nova convenit nostra planta." The first part of the sentence is very valuable, as it establishes the identity of the *L. Bærii* of Postels and Ruprecht. As to the second part, however it may have been with Areschoug's American specimens, the plant distributed agrees so completely with New England specimens that there can be no doubt that the Norwegian and New England forms belong to the same species. Farlow* gives a very careful account of the New England plant, and Kjellman † adds greatly to our knowledge of the Arctic forms of the species.

An interesting paper closely connected with this subject, and one to which I am indebted for many valuable suggestions, is one by Mr. P. A. Barber, entitled, "On the Structure and Development of the Bulb in *Laminaria bulbosa*." ‡ This paper has made possible a fairly satisfactory comparison between the earlier stages of *Laminaria bulbosa*, Lamour., and of *L. dermatodea*, De la Pyl., and helped to make the discussion of the relationship existing between the two species much more satisfactory.

Periods. — For convenience of description, the life-history of *Saccorhiza dermatodea* may be divided into four periods, each of which is characterized by some important changes in development.

First Period. — This period naturally deals with the development from the spore. The material is wanting for any satisfactory treatment, and as the plants are at first of microscopic size, these earlier stages will be discussed under the portion devoted to the histology.

Second Period. — 1. *Earliest Stages found.* — The smallest specimens available are two or three which measure 5 to 6 mm. in length. They were found growing in the same clusters with larger ones of the same species, and were detected only by very careful search. Smaller ones were sought for through each bunch collected, but none were found. A hand lens is necessary in examining these specimens. The point of attachment has been lost in every case. The stipe is distinct, and is about 1 mm. long and 0.14 mm. wide at the middle. It seems to be nearly cylindrical in shape, and expands gradually into the blade at the upper portion. The blade, which has thus a wedge-shaped base, is generally ovate or obovate, the broadest portion being in most cases about two thirds of the way from the base. The tip of the blade either tapers to a more or less acute point, or is blunt and truncated from having lost the terminal portion. Below, the stipe

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* N. E. Alg., p. 95.

† Arct. Alg., p. 223.

‡ Annals of Botany, Vol. III. No. IX. p. 41, February, 1889.

appears to be prolonged into the blade one third to one half the way up, as a sort of broad midrib. The midrib-like portion is rather wide at the base, and tapers gradually to a point. The edges are not straight lines, but are somewhat notched or toothed. As seen with the lens, the apex of this portion is not acute, but is somewhat blunt. (Cf. Figs. 1 and 2.)

The midrib is very striking in fresh specimens as it is of a deeper color than the rest of the blade. When examined with a low power (150 diameters), it is seen to be thicker and of more complex structure than the rest of the blade, which appears on focusing to be a simple membrane composed of a single layer of cells. The further details of this structure properly come under the sections devoted to the histology.

On some of these young specimens are to be found small clusters of hairs arising from the surface not only of the more complex portion, but also in some cases from the membranaceous outer part of the blade. These are the cryptostomata or "Fasergrübchen." By the presence of these organs the young plants of *Saccorhiza dermatodea* may be distinguished from the young plants of any of the other species of *Laminarieæ* of the New England coast, except from those of species of *Alaria*. From these they may be distinguished, after a little experience, by the outline and the color. *Saccorhiza dermatodea* in these early stages is usually elliptical to obovate, while the species of *Alaria* uniformly have a narrowly linear frond. The color of the young *Saccorhizæ* is light brown. They become somewhat greenish in drying at times, but generally take on a more yellow tint. The young *Alariæ* are of a much lighter brown, and become decidedly greenish on drying. The midrib-like portion in *Alaria*, too, is more linear in shape, and narrower, more like a real midrib. As soon as the *Alariæ* attain any considerable size the true midrib makes its appearance, and distinguishes them at once from the young plants of any of the other species.

2. *Later Stages.* — As the specimens become larger a number of changes may be noticed, which are well shown in a specimen about 3 cm. high. This specimen possesses a distinct organ for attachment, consisting of the slightly dilated basal portion of the stipe and a sort of small cushion by which this is attached to the substratum. The cushion has a spongy appearance and a dirty brown color, and differs decidedly from the stipe both in color and consistency. The stipe itself is about 3 mm. high and about 0.5 mm. in diameter. It is cylindrical in shape, and expands gradually into the lanceolate or

oblanceolate blade, which is about 6 mm. wide. The terminal portion of the blade has disappeared through erosion, but at the tip on either side are seen two narrow strips (cf. Fig. 3, E) of the membrane of the original blade still present. The rest of the blade is more complex in its structure. The cryptostomata are much more numerous and much more conspicuous. They are much larger towards the tip of the blade, and become smaller and smaller as they approach the base, until at the place where the blade passes over into the stipe they disappear altogether. Hence it is reasonable to assume that this transition place, as we may call it, the "Uebergangstelle" of German writers, is a region of active growth.

Third Period. — 1. *Development of the Rhizogen.* — Very soon after the primitive or simple membranaceous blade has thus been very nearly replaced by a blade of more complex structure, and the stipe has elongated to a somewhat greater extent, we come to the beginning of a set of changes in the lower portion of the stipe, which are of great importance in establishing the relationships between this species and others of the same group. The holdfast or organ of attachment in this stage differs from that of the preceding merely in its somewhat greater size. In some of the specimens, however, the holdfast is a vertically elongated body of narrowly conical shape. This variation seems to be the result of peculiar conditions in the substratum to which the plant is attached. The stipe in the specimen chosen as a good illustration of this stage (cf. Fig. 4) is about 8 mm. long and 0.5 mm. in diameter. It is for the greater part of its length cylindrical, but at about 2 mm. from the holdfast it appears somewhat swollen (cf. Fig. 4, B). This swelling, which is regularly ellipsoidal in general outline, is in the specimen chosen about 2 mm. in height and 1 mm. in diameter. Even before this swelling becomes evident, that portion of the stipe where it is to appear seems denser, and is therefore of a slightly different color from the neighboring portions, although at the time it is hard to detect that the surface is at all curved outward. The swelling or node is very readily seen, both in fresh and in alcoholic specimens, and is very nearly as distinct in specimens pressed for preservation in the herbarium.

This swelling is described by De la Pylaie in the "Flore de Terre Neuve" (pp. 49 and 50), and was observed by him in plants thrown ashore about the end of October. His description of a young plant is so excellent that I reproduce it here. "Tout le végétal n'avait alors que 2 à 3 centimètres de hauteur, et sa fronde, d'une délicatesse infinie, n'avait en largeur que 3 millimètres au plus. Cette fronde un peu réservée en pointe à son sommet puis ensuite linéaire sur la plus grande partie de sa longeur, s'amincit successivement jusqu'à se terminer par un petit stipe presque capillaire, où l'on distingue néanmoins, au dessus de son point radical, l'espèce de petit nœud (Rhizogène), que j'ai vu plus tard s'accroître et donner naissance aux principales racines qui fixent cette Algue aux corps solides." It is very evident from this description that De la Pylaie recognized this swelling just above the primitive discoid attachment as well as its function, and that he gave to it the name of "Rhizogène." In regard to this organ and the term applied to it, he explains in a foot-note as follows: "Organe exclusif à cette hydrophyte et au *L. bulbosa ;* il n'existe que chez ces espèces dans tout le règne végétal! n'ayant pas encore été désigné par un nom particulier, je propose celui-ci dont je me servirai pour éviter périphrases." This name, Anglicized to rhizogen, will be adopted in this paper to designate this organ. The blade in specimens in this stage varies from 3.5 cm. to 6.5 cm., and is perhaps at times even longer. It is narrowly cuneate at the base, and still bears some traces of the primitive blade at the apex (cf. Fig. 4, E).

2. *Development of the First Hapteres.* — For a number of stages now the changes which take place in the rhizogen are of particular interest. It increases, chiefly in diameter, until it projects out around the stipe in the form of a circular ridge, as shown in Figure 5 at B. This specimen is 7.3 cm. long. The holdfast is a disk-shaped body about 2 mm. in diameter. It will be best hereafter to distinguish this first organ for attachment to the substratum as the *primitive disk* or *primitive holdfast.* The rhizogen is situated about 2 mm. above this, and forms a conspicuous projecting circular ridge, about 3 mm. in diameter. Its upper surface is convex and rounded, while the lower surface is concave to a slight extent. Its projecting edge is coarsely crenate into five small lobes. The stipe in this specimen is 7 mm. long and 1.5 mm. in diameter. The base of the lamina is narrowly cuneate, as in the preceding period, but the blade itself is more lanceolate, occurring very linearly lanceolate in some specimens. A trace of the primitive blade (cf. Fig. 5, E) still lingers in some specimens. The cryptostomata are very abundant in this stage.

As the plants increase in size the rhizogen continues to grow. It increases in diameter proportionally with the stipe. The lobes, scarcely noticeable at the beginning, grow out into finger-like processes (cf. Fig. 6, F), which extend out at first nearly horizontally, and then more and more obliquely downwards. Figure 6 represents a specimen in this stage; its length is 13 cm. The rhizogen is 5 mm. from the primitive disk, which is slightly larger than in the last specimen described, but not otherwise different. The rhizogen itself is about 4 mm. in diameter. It has several lobes of some length, which are already started downward. The blade presents no particular differences in form, but in specimens of this stage it is very rare indeed to find any trace of the primitive blade remaining.

In somewhat older specimens the finger-like projections have reached the substratum, have flattened their tips against it, and have become attached to it. There are usually five projections, and they form a whorl of attaching organs, which constitute the second holdfast. They are called hapteres by most recent writers,* after the term used by Warming † to designate very similar organs in the *Podostemaceæ*. The hapteres form a regular whorl (cf. Figs. 7 and 9), and their points of attachment form a circle about the point of attachment of the primitive disk (cf. Fig. 8). The development of the hapteres marks the end of the first stage of what is to be the permanent holdfast of the plant, and confirms De la Pylaie's statement quoted above.

3. *Development of the Second Hapteres.* — In the next series of forms, the second and last stage of the permanent holdfast is formed in a manner essentially the same as that in which the first stage was developed. On the rhizogen above the primary whorl a new whorl of protuberances appears. These protuberances are in most cases regularly alternate with the hapteres of the first whorl, but may at times be so placed that one or more of this set are situated above similarly placed hapteres of the first whorl. While the new hapteres are developing, the older hapteres increase in length, and on this account come to occupy a more upright position (cf. Fig. 7 with Fig. 9). The new hapteres, therefore, have the opportunity of growing down obliquely, and of attaching themselves to the substratum, after the manner of those of the first set. Their points of attachment form a second but rather irregular circle outside the one made by the ends of the primary hapteres. We now have three sets of attaching organs: first, the primitive disk; second, the primary whorl of hapteres, all of which are usually present at this stage; and third, the secondary whorl of hapteres. It often happens that some of the hapteres of the second set remain as mere protuberances after the rest of

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* Foslie, Die Lam. Norwegens, pp. 6 and 7, 1884. Barber, Annals of Botany, Vol. III. p. 48.

† Bot. Zeit., Bd. XLI. pp. 193 and 197, 1883.

the members of the whorl have reached the substratum and have become attached. This generally occurs at a place where two of the hapteres of the first set remain close together. In such a case the secondary hapteres may never develop at all, and their place may be permanently supplied by members of the first whorl. But, as a general rule, all the hapteres of this second set reach their full development, and constitute the important part of the permanent hold-fast. The smallest specimen examined which shows the protuberances that are to grow out into the secondary hapteres is 16 cm. long, while one that has reached a length of 30.5 cm. has most of the second set attached, but many of them only slightly. In this specimen the primitive disk has entirely disappeared, and there are five hapteres of the first set, which is apparently the original number. Of the second set only two are firmly attached; three are just touching the substratum; and there are two more just showing as small protuberances from the disk of the rhizogen. The stipe of this specimen is 5 cm. long and 3 mm. in diameter at the base. Below, it is cylindrical, but in the upper portion it is noticeably flattened. Even in a specimen of this size the stipe expands gradually into the blade, which in what seems to be the most common form in New England is broader in proportion to the length than in previous stages. This blade is elliptical-lanceolate, 25.5 cm. long and 4.8 cm. wide in the broadest part, which is about half the length from the base. The cryptostomata are very abundant and very conspicuous.

All of the previously mentioned forms were obtained from the pools at Nahant in the gatherings made on April 24 and 25, 1889. The two or three largest and most developed specimens came from below low-water mark, while the younger specimens came for the most part from the uppermost pools. On May 12, some specimens collected from the higher pools were about as large as the largest specimens of the first collection.

On May 25, a few specimens were collected at Peak's Island, Maine, the measurements of some of which are given in the following table: —

No.	Length of Stipe. cm.	Length of Blade. cm.	Width of Blade. cm.
1	3.2	15.9	1.6
2	5.1	26.9	1.4
3	4.45	26.7	1.6
4	10.8	55.9	1.9
5	10.2	35.6	1.9
6	10.2	99.1	3.8

No.	Length of Stipe. cm.	Length of Blade. cm.	Width of Blade cm.
7	11.4	85.1	3.2
8	9.5	85.1	5.1
9	9.5	56.5	3.5
10	15.2	85.1	3.2
11	12.7	76.2	3.3

As can be seen from the above table, which represent specimens taken at random, all the plants of this collection are remarkably long and narrow. The blade of No. 1 was broken off short, as if by some accident. The tips of the rest were eroded in the customary fashion. Nos. 1 to 9 were found growing in a shallow pool just above low-water mark, while 10 and 11 were found cast ashore on a small beach not far away. All of them were of a remarkably light yellow-brown color, and very pellucid for specimens so long as some of them were. About thirty specimens of much the same character were collected at this locality on the same date. All sorts of transitions between this narrow form and the more ordinary form are found. I have seen plants of this narrow form at Nahant and Marblehead also, but they were few or single, and this is the only time that I ever found so many together.

Fourth Period. — 1. *Transitional Forms.* — Some specimens were collected at Nahant, June 12, 1889, which show some very striking peculiarities. The specimens, between twenty and thirty of which were carefully examined at the time, were all about the same size, and apparently of about the same age. They grew not only just below low-water mark, but in the highest pools as well. They were all in the neighborhood of 55 cm. long. The holdfast was well developed, and the hapteres were stout and of a dark brown color. The stipe was decidedly flattened above, and from 6 to 10 cm. long. At the top where it passes over into the blade there is a noticeable ridge made by the abrupt transition from the thick stipe to the much thinner blade. The stipe has become a very dark brown, and is opaque, having lost entirely the translucent appearance characteristic of the organs of the younger plant. But the most noticeable and interesting change is one which is to be seen in the blade itself. In the upper part of this the color is still decidedly yellowish, and the cryptostomata are abundant and conspicuous; but toward the base there is a noticeable transverse constriction (cf. Fig. 11, A), and below this the blade is of a dark brown, agreeing more nearly with the stipe in color, and almost if not entirely destitute of cryptostomata. The cryptostomata grow smaller and smaller as they approach the constriction and disappear at a small distance above it. Below the constriction not a cryptostoma is to be seen. The outline in the figure just referred to above was traced from the plant itself while fresh, and is to be compared with Figure 10, in which the permanent oar-shaped base of the adult plant is represented.

As the blade grows older and the part below the constriction increases in size, the constriction gradually disappears. In a specimen of this same collection, 73 cm. long, the last traces of the constriction are to be seen at about 10 cm. above the base of the blade. The base of the blade now becomes more blunt, and begins to take on the shape of the base of the blade of an oar, which is very characteristic of the adult plant. The distinction between stipe and blade becomes for the first time sharply marked.

This process resembles in almost all respects the process of renewing the blade so well known now in the European species of *Laminaria*,* and seen by the writer in most of the species of *Laminaria* and *Agarum* of New England. But in this process the old blade, which is thick and is fruiting or has fruited, is cast off, and is succeeded by a new blade of more delicate consistency. In *Saccorhiza dermatodea*, on the contrary, as shown more fully below, the new blade is thicker and denser, and destined to bear the reproductive organs.

It is about this time in its life-history, also, that the plant grows most actively and reaches its maximum of size. The largest specimens I have ever found were growing at Peak's Island, June 28, 1888. The largest specimen of my collection of that date measures 142 cm. when dried. The stipe is 16.5 cm. long, and the blade reaches a width of 12 cm. Hundreds of plants of this size, and even larger, were growing in that locality at that time.

Farlow says in his New England Algæ,† that the stipe sometimes reaches a length of two feet, and the blade a length of six feet. The figures are probably taken from Eastport specimens, where the species is said to grow more luxuriantly than it does farther south. A specimen in the herbarium of Mr. F. S. Collins of Malden, Mass., collected at Eastport in August, was in this same stage of growth. The stipe measured 66 cm. The blade was short and fragmentary, but measured 21.4 cm. in width.

In these large specimens the blade is very thin and papery on drying. The color is still a rather yellowish brown, and the cryptostomata

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* Cf. Le Jolis, Examen I., p. 549, 1856; Foslie, Die Lam. Norwegens, p. 23; and earlier writers.

† Page 95.

on the upper part are more numerous and more conspicuous than at any other stage. They are larger in these fronds than at any time previous, as will be noted below. In the basal third or half of the blade, however, the cryptostomata are entirely wanting. The color of this portion is darker, and it is thicker and more leathery.

The stipe is more flattened at the top, and the holdfast is larger and firmer. Occasionally one is found in which one or more of the hapteres is branched. The branching, however, is only a simple forking of the haptere, and may perhaps be regarded as indicating two hapteres, fused together above but free below. This branching, as far as my experience goes, is decidedly rare.

At about this period, and in some cases also somewhat earlier, the blade splits vertically into two or more divisions. Two segments seems to be the rule in the narrower blades, but in the wider ones there are generally three. I have seen a number of specimens where there were four, and in the herbarium of Mr. Collins I have examined one in which there were five. The splits are continued almost to the very base of the frond, and the segments are more or less strap-shaped. The old fronds split very readily in this vertical direction, and one often finds them cast ashore in the springtime split down to the holdfast itself. In Mr. Collins's herbarium there is a specimen which had been split down thus far when young, and each half had proceeded to continue growing, and there are two more or less perfect plants in that case from the same holdfast. It reminds one of the famous bifurcate specimens of *Laminaria digitata*, of which a summary is given by Le Jolis.*

2. *Adult.* — As the season progresses, the plant ceases to grow so actively as at first, and the tip wears away faster than it is renewed. Consequently, the plant becomes shorter as the summer advances, but it also grows thicker and denser. I have unfortunately no specimens collected early in July, but through the kindness of Dr. G. H. Parker of Harvard University I have some excellent specimens collected late in July. These are shorter than the earlier specimens, are of a dark brown color, and very leathery. They show no traces of cryptostomata. In September I collected very similar specimens at Nahant with zoosporangia just forming. In October, specimens with well formed zoosporangia were not uncommon at the same place. Fruiting specimens of this species may be found from October on until May of the next year.

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* Examen I., p. 540.

Kjellmann says * that the proper season for the formation of zoospores in this species is in September or the beginning of October, on the Norwegian coast. At Spitzbergen he found specimens with zoosporangia in July and August, and at Nova Zembla in July. There is apparently in the more northern regions an earlier ripening of these bodies.

The fruit occupies about the lower half of the blade in the well developed specimens. The collection of sori, or cloud-like patches of fruit, covers the surface on both sides at the very base of the frond, but separates above into irregular-shaped blotches of considerable size. When the water has evaporated from the surface of the frond, these sori have a peculiarly soft and velvety appearance, and are of a somewhat lighter brown color than when wet. When dried, the mature plants are of a decidedly black color, but the sori are even blacker than the frond, and may thus be detected readily even in herbarium specimens.

De la Pylaie † describes the fruit as entirely covering both surfaces of the frond, and as occurring toward the end of autumn. Areschoug ‡ says: "Fructificatio . . . non format maculas extensas l. fascias, ut in Laminariis, sed maculas minutissimas fere punctiformes, nunc separatas, nunc approximatas, quo fit, ut cum siccata est, lamina farina nigrescente conspurcata videatur." The specimens from the New England coast do not agree with this description, as may be seen from what has been said above.§

Specimens are cast ashore in the greatest numbers from November until May. I have generally found them most abundant in February. A specimen thrown ashore at Lynn, Mass., February 9, 1890, was in very perfect condition, and so will serve as a good illustration of these very old plants. The lower part of this specimen is represented of the natural size in Figure 10. It measured 70.5 cm. in length, and the holdfast was about 2 cm. in diameter. The primitive disk was still present, although much shrivelled and wrinkled. Of the first set of hapteres three were present in a good state of preservation on one side, and the places where the other two had been were to be seen on the other. There were nine hapteres present in the outside set. All the hapteres were unbranched. The stipe was 12.1 cm. long. It was cylindrical at the base and flattened at the top. The blade had the

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* Arct. Alg., p. 225.

† Fl. Terre Neuve, p. 49.

‡ Obs. Phyc., Part. III. p. 12.

§ Cf. also Kjellman, Spetsb. Thall., II., p. 14, 1877.

oar-shaped base characteristic of these old specimens, and expanded gradually until it reached the truncated apex. It was 58.4 cm. long, and 12.7 cm. wide at the top.

A curious thing to be observed in the specimens cast ashore is that the great majority of them lack the holdfast, although the attachment by this organ does not seem to be a very firm one; for if one catches hold of a growing plant, even by the tip of the blade, and gives it a strong and sudden pull, it almost always comes away from the substratum uninjured, offering in this respect a strong contrast to the ordinary species of the *Laminarieæ.* But the majority of the old specimens cast ashore in the spring look as if they had been twisted off at the lower end of the stipe, and occasionally a bunch of fronds will be found cast up, all twisted together in a most complicated manner.

This species appears to be an annual. De la Pylaie * and Areschoug † were also of this opinion, and all the data that are at hand seem to support it. On the coast of Massachusetts I have never seen an adult plant after May (when old, decaying, fructified specimens were cast ashore) until September. The plants growing in the pools become very battered and torn, and covered with parasites in December and January; and the adult plants found in the springtime are always very old and about to decay. There is, besides, no indication in the structure that the plant is either biennial or perennial.

Summary. — From what has been said above, it will appear that each of the four periods into which the life-history has been divided for convenience has its characteristic features.

The lack of suitable material, and the small size of the germinating plants, prevent any satisfactory discussion here of the changes taking place in the first period and the early portion of the second. Toward the end of the second period, however, the young plant is provided with a distinct disk for attachment, a short cylindrical stipe, and a blade which for the most part is more than one layer of cells thick.

The third period has for its characteristic feature the development of the permanent holdfast. A small swelling, the rhizogen, appears a short distance above the primitive disk, increases in size, and produces two whorls of short fibres, the hapteres, one above the other. The hapteres attach themselves to the substratum by their tips.

The fourth period extends to the death of the plant. In all the preceding stages the base of the frond has been narrowly cuneate, and

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* Fl. Terre Neuve, p. 49.

† Obs. Phyc., Part. III. p. 12.

it has been difficult to determine either where the stipe ended or where the blade began; but at the beginning of this period occurs the process compared above to the process of the renewing of the blade in other *Laminarieæ*, after which the boundary between stipe and blade is well marked, and the blade itself becomes thicker and firmer, and ceases to possess cryptostomata. When this set of changes has fairly ended, the zoosporangia are produced, and the plant, having served its purposes, dies, and gives place to a new generation.

HISTOLOGY.

Having thus considered with some detail the various morphological changes which *Saccorhiza dermatodea* undergoes in the course of its life-history, we are in a position to turn to the histological changes which take place during the same period.

Literature. — The histology of this species has been seldom referred to. De la Pylaie's account [*] does not express to us any very definite idea. Areschoug [†] has described the structure of the cryptostomata and of the organs of fructification. Kjellmann [‡] has spoken of the structure of the stipe, and especially mentioned the "very long tubular cells, with very thick walls," found in this organ in this species, and lacking in the *Phyllaria lorea* found by him at Spitzbergen and Nova Zembla. Barber, as mentioned above, has described the histological changes occurring in connection with the development of the bulb in *Saccorhiza bulbosa*, De la Pyl., and has thus furnished a valuable means for comparing these two species.

The account of the histology will be arranged according to the periods of development sketched out above.

First Period. — The first period begins with the zoospore and its germination to form a filament of a single row of cells, and extends to the formation of a membrane of a single layer of cells in thickness. No plants of *Saccorhiza dermatodea* belonging to this period have been seen, but evidences of the existence of these early stages are present in the youngest plants known.

As far as I know, Thuret [§] is the only one who has described or figured either the zoospores or germinating plants of any species of the *Laminarieæ*. He figures the entire development of *Saccorhiza bulbosa* [||] for this period, as well as the early stages of *Laminaria*

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[*] Fl. Terre Neuve, pp. 50 to 52.

[†] Obs. Phyc., Part. III. p. 12.

[‡] Arct. Alg., pp. 224 and 225.

[§] Ann. Sci. Nat., Ser. 3, Tom. XIV. Pl. 29 and 30, 1850.

[||] *Loc. cit.*, Pl. 30, Figs. 5 to 10.

saccharina.* Kützing† figures and describes young plants of *Laminaria saccharina* consisting of a simple membrane. I have seen a young plant, probably belonging to *Laminaria Phyllitis*, (Stackh.) J. Ag., which consisted of a simple filament.

It seems fairly certain, then, that the germinating zoospore of the *Laminarieæ* gives rise first to a simple filament, and later to a simple membrane; and it seems very probable also that the earliest stages of *Saccorhiza dermatodea* will be found to correspond very closely to those known for *Saccorhiza bulbosa*.

Second Period. — The preceding period is doubtless very short, and changes soon begin which convert the simple membrane into a membranaceous frond of more complex structure. The changes take place in the early portion of what has been marked off as the second period of the development. The youngest specimens in my possession show these changes already well advanced, and have been partially described above in the account of the morphology. They are of very delicate consistency, and are therefore difficult to manipulate. Furthermore, there were only two or three of the very small ones, and on these accounts many of the details of the histology here given had to be derived from somewhat older plants, belonging however to the same period.

When one of the youngest plants is examined under a low power (150 diameters), it is seen that the stipe and the midrib-like portion of the blade have already arrived at some degree of complexity of structure. The outline of this midrib portion, as mentioned above, is irregular (cf. Figs. 1 and 2). In Figure 1 it is seen to have several tooth-like projections from the main portion. One of these (labelled A) is situated at the tip. Somewhat below, at A′, there is another one, and at A″ still another. These are only more prominent than the others at A‴, and so on, but do not differ in kind. At the very tip the blade is eroded, and consequently we find here, as has been described for other *Laminarieæ*, that the growth is not apical, but from below, and that the apex of the blade is the oldest portion. As a still further evidence of this, it can be seen that the apical portion of the blade is of simpler structure, and becomes more complex downward. This is exactly what we should expect from what we know from other members of the group. Consequently, a set of transverse sections of one of the plants, arranged in a series from above down-

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* Ann. Sci. Nat., Ser. 3, Tom. XIV. Pl. 30, Figs. 1-4.

† Phyc. Gen., p. 345, Taf. 24, I, Fig. 5, 1843.

wards, will throw a considerable light on the changes of structure which it has undergone in its previous development. In such a series, projecting portions, such as A', etc., are of significance in showing that the growth in complexity from the simple membrane did not originate from one point and extend out regularly, but originated at several points irregularly situated. A comparison between Figures 1 and 2 will also show this.

To get these sections some series were made by hand with the razor, and more complete ones were cut on a microtome from specimens which had been embedded in paraffine. Some of the latter were from specimens which had been treated with corrosive sublimate. They were stained with Kleinenberg's hæmatoxylin before being embedded, and mounted in balsam after they were cut. Some of the series gave very good results, others were very much shrivelled.

The upper portion of the blade, or the primitive blade as it is convenient to term it, is but a single layer of cells thick, as appears in sections as well as by focusing. As seen on the flat surface of the blade the cells are nearly square or slightly rectangular, but in some cases elongated in the direction of the long axis of the blade. In transverse section they appear nearly as thick as broad, but they vary much in this respect. The cells contain a number of large and conspicuous lenticular chromatophores, usually arranged about the inner walls. The protoplasm in these cells is in the form of a thin film lining the wall. The nucleus is not very conspicuous, and is hard to demonstrate. These cells possess all the characteristics of age, and have probably ceased to take any active part in the growth of the plant.

On the one-layered portion were found in some of the specimens the small clusters of hairs already alluded to. Attempts to get a good section through such a bunch were fruitless. As far as could be seen by focusing, the hairs protruded only on one surface, and were generally five or six in number. When viewed from the other side from that on which they were situated, they were seen to arise from basal cells formed from the divisions from one (or at times from two) of the ordinary cells of this portion of the blade. The basal cells of the hairs are almost isodiametric, are densely filled with protoplasm and chromatophores, and possess a single large nucleus. Farther up, the cells become elongated in the direction of the long axis of the filament; the protoplasm becomes filled with large vacuoles; and the nucleus becomes central, and connected with the peripheral protoplasm by fine threads. At the distal end the cells are four to six times as long as broad, and are destitute of contents. These hairs accordingly have the region of active growth at the base, as do most of the hairs in the *Phæosporeæ.*

In the series of sections the first evidence of an increase in complexity is shown in Figure 12. In this transverse section it will be seen that two cells, at A and A, have divided by walls parallel to the surface of the frond, and that these two cells are not situated side by side, but are separated by one cell. Sections from other plants represent the initial cells somewhat differently. In one case there was a single one, and in another two were side by side. A section from the same series as the one represented in Figure 12, and about 30 μ below it, is represented in Figure 13. In this the process has gone further, and the central portion of the blade is two-layered, while the edges are only one-layered. A longitudinal section of a young blade showed that in that particular specimen the two-layered portion was five cells in height. Soon we come to a section such as that represented in Figure 14, where there is a third cell of different shape and appearance in the centre, and the two layers are separated from each other in the middle to make room for it. This cell lacks the chromatophores, is round in cross-section, and has a lining of dense protoplasm, in which are embedded numerous small nuclei, which take on a deep stain with hæmatoxylin.

In the same figure will be noticed two groups of hairs, one projecting from each surface. Each group seems to have arisen in this case from the divisions of a single cell. In the several-layered blade they are frequently opposite in this fashion.

Figure 15 is drawn much less magnified, and the cells are all represented on one side to show the proportions existing between the many-layered and the one-layered portions of the blade. It will be seen here that there are three of the central cells in this section. In longitudinal section these central cells appear as elongated tubes, the ends of which are not readily found. They will be spoken of as tubes, or tubular cells, for the present.

Figure 16 shows a section still lower in the original series. The many-layered portion is wider, and the cells appear irregularly placed; but the arrangement is seen better in Figures 17 and 18, still lower down. The tubular cells are readily seen at *a* and A. The many-layered blade, about half of which is represented in the figures, has increased chiefly in width. At B in Figure 17 is seen a group of four cells, situated apart in the one-layered portion, which recalls the state of things represented in Figure 12, and looks as if the cells were the initial cells of a new many-layered portion. Such is the case in fact.

This is the origin of the tip of such a portion as that labelled A″ in Figure 1. At B in Figure 18, about 30 μ below the section figured in the preceding, this group of four cells has increased by dividing to form six. The divisions are repeated, and this portion grows wider until the intervening space is traversed and it unites with the main part.

This fact is significant in indicating that there is no one cell, nor even one region, whence all growth proceeds, but several cells and regions, and these somewhat irregularly placed.

As we go down, the outer cells, one by one and at first somewhat irregularly, divide into two by a wall parallel with the surface of the frond, until at length we have a layer of smaller cells on each side, a layer of large cells adjoining each of these, and the tubes in the middle. The outside layers on each side may be called the limiting layers (L in Figs. 19 and 20) ; the next layers, of larger and more irregular cells on each side, may be spoken of as the cortical layers (C in Figs. 19 and 20) ; and the tubes alone represent what later demands attention as the medulla.

The lower portion of the blade does not increase in complexity for some distance, but widens until the whole width of the blade is occupied by the many-layered portion. But in the region where the blade narrows and passes gradually over into the stipe, in what has been spoken of above as the transition place, a new set of structures arises, which are intimately concerned with the thickening of the blade and stipe, and the increase in the complexity of the tissues. The fact that this set of changes originates in this portion shows that the principal meristematic region is situated here in this species, as it is in others of the same group.

At the transition place in such specimens the limiting layer is distinct, and consists of rather small cells of nearly equal dimensions in the three principal directions. The cortex has two, or even three, layers of two more or less distinct kinds of cells. Those of the outer layer are like the cells of the simple cortical layer. The inner cells appear in transverse section much like those of the outer layer, except that they are more rounded and lie more separated both from one another and from the outer layer, and in the middle layer among the tubes. In longitudinal sections, however, they are seen to be much more elongated than the outer, some of them being five to six times as long as broad. From them, too, are given off short hyphal branches, which extend out laterally from the cells, and protrude into the middle portion. It was impossible to see the mode of origin of these hyphal branches in the one or two specimens of this period which showed them, and so a more complete account of them is left until the next period is discussed.

The stipe, towards the end of this period, becomes a rather solid structure, composed of the following tissues. Outside is a limiting layer similar to that described for the blade, but which is in a state of more active growth. The cells composing it are somewhat elongated radially, and divide actively by tangential walls. By divisions in the two directions perpendicular to this, it also keeps pace with the growth of the stipe in circumference and length. Within this are several layers of cortical cells, and the centre is occupied by a mass of elongated tubes. No hyphal cells are present except at the transition place.

All except one of the younger specimens had lost the point of attachment. This individual is 6 mm. high. The base is decidedly bulbous, and is 18 mm. wide, while the stipe above is about 0.1 mm. wide. The bulbous base is about 0.13 mm. high. At the bottom it is attached by a number of hair-like bodies, which it seems proper to term rhizoids. These are comparatively numerous (probably between 50 and 60), and arise as prolongations from the cells of the limiting layer of the basal portion of the enlargement. The rhizoids themselves are irregularly cylindrical, and at this stage seem to be for the most part unicellular. Toward the distal end the shape is more irregular, the wall thicker and wrinkled, and at this portion too they are not infrequently and somewhat irregularly branched. The branches are very short and the tips of the rhizoids are somwhat swollen. This specimen was growing among a mass of other young plants and fine filamentous forms of other species, and this allowed the rhizoids to be seen to greater advantage.

The above description is to a certain extent fragmentary, but much of that is due to the character of the available material. That previous to this period there exist stages in which the frond consists of a simple membrane of a single layer of cells seems to be evidenced by the fact that, in the youngest specimen seen, the blade is for the greater part in that condition. It is supported, too, by what we know of the early stages of some nearly related species. What the stages are by which the development proceeds from this simple frond to such a stage as that represented by the youngest specimen described is largely a matter of conjecture. That the complexity comes about by a series of definite and gradual changes seems probable. It is supported, moreover, by what is described above. For in the blade we find at the top, which is the oldest portion, the simplest structure of a single layer of cells. It then becomes two-layered, three-layered, four-layered, five-layered, and finally still more complex by the growth of the hyphal branches.

That the stipe develops somewhat differently is evidenced, not only by its different structure, but also by its different shape. In the absence of a series of earlier stages to indicate the way in which the complexity came about, we have almost nothing to help us ; for in a specimen only 6 mm. long the stipe is 12 or 13 cells in diameter. We get a slight clue, however, from a young specimen of *Laminaria Phyllitis* collected at Nahant. In this the stipe consists of a central vertical row of cells and a cylinder of cells about it only one layer thick, so that a transverse section is only three cells across. This seems to indicate that changes to produce the stipe have followed something of the same course that has been followed in the blade, but have been modified in such a way as to produce a cylindrical rather than a flattened structure.

Kützing* figures some details of the development of *Laminaria saccharina* during this second period. Reinke† also mentions the partially one-layered stage of the same species, and gives a rough sketch of it.

Third Period. — The most important feature of the third period, as marked out above, is the development of the rhizogen and the two whorls of hapteres. At the same time, the blade and stipe increase greatly both in size and complexity. The early stages are almost exactly like the later stages of the previous period, except for the development of the swelling which marks the appearance of the rhizogen. It will be best, therefore, to describe first the changes in structure which accompany this.

A longitudinal section through a very young rhizogen shows that the central portion consists wholly of elongated cells arranged in vertical rows. There are no long tubular cells present in this portion. The changes which result in the swelling begin at the centre and proceed outwards. The very central cells increase greatly in diameter, and are followed in this by the outer rows. They tend also to increase in length, but, being hemmed in on all sides, soon have the appearance of being cramped. This process, thus taking place in a certain definite region of the stipe, causes the sides to bulge outwards,

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* Phyc. Gen., p 345, Taf 24, I, Figs. 1 to 6.

† Pringsh. Jahrb., Bd. X. p. 375, Taf. XXVII. Fig. 18, 1876.

and the swelling called the rhizogen results. It is produced by the great increase in the size of the cells, not by any large increase in the number of cells, as Barber* has already described for the same organ in *Saccorhiza bulbosa.*

Not only do the inner cells of the rhizogen enlarge, but the walls thicken and separate from one another, except at certain points on each face, where they still remain united. The space between the separated walls is filled for some time with a mucilaginous modification of the outer layers of the cell wall (cellulose) ; but after a while it is impossible to detect anything of this kind, and the substance probably becomes very watery indeed. However that may be, the spaces between the walls finally become filled with small cells in lines and rows, the origin of which is not readily determined. They appear to bud out from the larger cells in the form of small hyphæ, which, however, become so crowded that they seem to form a compact tissue almost at once, and to lose all trace of their hyphal structure. (Cf. Fig. 21, *b.*)

The limiting layer has continued growing, and at certain places along the equator of the rhizogen, in company with the underlying cortical cells, it takes on a much greater activity than it does elsewhere. The increase at these portions is in the radial direction, and is brought about both by the tangential division of the cells of the limiting layer and by the increase of the cortical cells in the radial diameter. As a result several protuberances are formed in the zone of the equator destined to push out into hapteres. The cortical cells increase to from six to eight times their original radial diameter, and, new cortical cells being supplied by the activity of the limiting layer at the distal end of each protuberance, the haptere begins to elongate. The limiting layer is more active at the summit of a haptere than along its sides ; in fact, very few new cells are formed in the latter region at first. Later, however, when it has finished its growth in length, these conditions are reversed, and its growth is then in thickness. When the haptere has reached the substratum in its outward and downward growth, the cells of the limiting layer along the surface in contact with the substratum grow out into rhizoids for attachment like those mentioned in the case of the primitive disk.

The second set of hapteres arises after the first set is fully formed. They develop in exactly the fashion that the members of the first set did.

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* Annals of Botany, Vol III p. 55.

This brief sketch shows how the rhizogen with its two sets of hapteres develops. They do not increase in complexity to any extent during this period. But while this has been taking place there have been important changes in the other organs of the plant.

If we start at the tip of the blade of a specimen which has the first set of hapteres well developed, we shall find it to possess a well defined limiting layer on each surface, and within this, on both sides, a cortical layer of a single series of cells, and in the centre the medulla, represented by a few scattered tubes. As we approach the base, we find the limiting layers more and more sharply defined. Their cells are smaller and more elongated radially, and give evidence of greater activity. Within these the cortical layers are more developed, and are to be distinguished into an inner and an outer layer. The outer layer consists of smaller parenchymatous cells, while the inner contains larger elongated cells. We have, too, at this point a distinct medulla, in which the long tubular cells form a conspicuous element. Surrounding them are elongated tube-like cells of an appearance intermediate between that of the original tubes and the elongated inner cells of the inner cortex. Their walls are thin, while the walls of the original tubes are now noticeably thickened, and they are in general destitute of the dense contents of the latter. They have attached to them and entwining about them numbers of hyphal filaments, which usually have a lateral or oblique direction of growth.

If one examines the innermost rows of cells of the inner cortex in transverse, or better in longitudinal section, he will see whence these hyphæ arise. As the cells of the inner cortex elongate, the middle layer of the common wall becomes swollen, and the cells become finally separated from one another, except at a few points on each face. As the layer continues to swell and to become indistinct, the connections at these points become drawn out into short tubes; and since the process continues, these may become quite long at times. The tubes or hyphæ may be known as connecting hyphæ (Verbindungshyphen). In the other *Laminarieæ*, as far as investigated, they are said to arise only at points on the walls where there are pits, and this seems to be true of the specimens examined; at any rate, in all places where the point of origin could be plainly seen, this was the case. In the region where the cells begin to separate, the cell walls proper are thin, and the pits are not conspicuous. But if the section be stained with a dilute solution of Boehmer's hæmatoxylin the appearances shown in Figure 23 are brought out. In this figure it is seen that at the place where the two cell walls remain in contact there is a thickening which takes on a deeper stain than the comparatively thin walls do. In Figure 23, also, one of these thickenings shown in surface view is seen to be in the form of a ring. In cells which have separated more, and have a connecting hypha, there appears to be just such a thickening at the point in the hypha which represents the place of contact in the originally adjacent cells.

On the longitudinal walls of these inner cells of the inner cortex may also be seen small rounded protuberances which grow out into hyphæ. These hyphæ, which in contrast to the connecting hyphæ may be called free hyphæ, grow horizontally inwards, and twine among the separated elements of the medulla. They sometimes arise from pits, and probably always do, although this was not to be plainly seen in all cases. The hyphæ when just starting do not seem to have a thickened ring at the base, but nearly all of the longer ones do. There seems to be no fundamental distinction between free hyphæ and connecting hyphæ. A connecting hypha may be separated from one of the two cells, either at the middle or at one end, and, thus becoming a free hypha, continue its growth. Where, too, the free hyphæ originate as small protuberances, it is probable that at these points had been situated pits, but that the two cells had nevertheless entirely separated from each other.

The reason why the cells of the medulla and inner cortex become separated from one another is not at all apparent. It is suggested that these cortical cells, growing rapidly in length, become longer than the corresponding region of more external cells, and so, becoming somewhat bent, have a tendency to separate except at places where they are most firmly attached, viz. at the pits. This would seem to go a step farther in the medulla than it does in the inner cortex. In the former the cells separate almost entirely from one another, except as they are united together by the connecting hyphæ, and, the ends being free to slide up or down, the elements can elongate to a much greater extent than they could when they were members of definite vertical rows.

We find, then, at the end of this period, four sorts of cells in a medulla of this stage, viz.: first, the original tubes; second, the tubes arising from the elongation of the cells separated off from the inner cortex; third, the connecting hyphæ; and fourth, the free hyphæ. The further changes in the medulla introduce no new kind of elements, but are brought about by the addition of new elements of the last three kinds, and the changes which these undergo.

The development of the cryptostomata may be readily investigated in the thicker blades at this stage of growth. A series of sections at and a little above the transition place will give all of the early stages. The first indication that a cryptostoma is forming is the appearance of a shallow saucer-shaped depression. This will be seen to be due to the fact that the cells of the limiting layer in the region of this depression cease to divide as actively in a tangential direction as they have been doing, or as actively as their neighbors are doing. Furthermore, the cells of the outer cortex immediately below this point do not increase in size either so rapidly or to so great an extent as their neighbors do. So very soon this region is left behind by the more active growth of the rest of the blade, and forms a slight depression.

Very soon also the cells of the limiting layer at the bottom of this depression begin to grow out into filaments, and a stage of this is represented in Figure 22. In this drawing the filaments or hairs are only three or four cells in length, and still possess the original rounded terminal cell. The growth is at the base, as may be seen from the figure, and as was described in the cases of the clusters of hairs found on the primitive blade. The oldest cryptostomata of specimens of this stage are decidedly bowl-shaped, but they lack entirely the prominent overhanging margin to be found in older specimens.

Fourth Period. — Transitional Forms. — Having developed the permanent holdfast, the plant enters the final period of changes. Early in this, its active vegetative life ends, and it begins to mature and to ripen. At the very beginning, it starts to throw off the old blade, which has been, by means of its thinness and abundant cryptostomata, so well adapted for obtaining nourishment and for assimilating it, and proceeds to develop a frond especially adapted for bearing the reproductive bodies.

Through an oversight, specimens of the stage showing the renewal of the blade were not preserved otherwise than as pressed for the herbarium, and so I am unable to give an account of the stage where the transition takes place. But the change is brought about by a thickening of the walls and a modification of the contents of the cells, rather than by any change in the kinds of elements or in their distribution.

As mentioned above, the growth of the blade is very rapid at about this time, and at the boundary of these two periods the plant attains its maximum length. The most striking thing, perhaps, about one of these large plants, such as were collected at Peak's Island and at Nahant in the latter part of June, is the abundance and size of the cryptostomata. It is in these plants that they reach their final complexity, for in the new blade just forming they are entirely absent. They are saucer- or shallow bowl-shaped depressions, about 0.3 mm. in diameter, 0.15 mm. deep, with a large number (60 to 70) of hairs projecting from the bottom. The margin of the saucer has a sort of rim projecting in over the edge of the depression, such as Areschoug* describes for the Norwegian plant.

Adult Forms. — Specimens collected by Dr. Parker at Nahant, on July 26, 1889, are shorter than the last, have no cryptostomata, are of a darker color, and more leathery in consistency. Sections through the various organs of some of these specimens show the arrangement of tissues much as described in the last; but show also that the walls of all the elements of these tissues have undergone extensive thickenings, and that the elements themselves are somewhat larger. It will be well to glance, then, at the changes which have thus taken place in the tissues of a plant more matured, but not yet fruited. Such plants are common at Nahant in the middle and latter part of September.

a. Limiting Layer. — In these plants the limiting layer is still present, but is covered with a thick secretion resembling a cuticula. The latter may be separated readily from the section, and then has a pitted appearance where it has been parted from the rounded ends of the cells. The cells of the limiting layer, both in stipe and in blade, are usually somewhat elongated radially (cf. Fig. 24, L). The very outside walls and the cuticula give a yellow reaction with chloriodide of zinc solution, but the inner walls turn a pale bluish. At the base of most of the cells small cells may be seen in cross-section (cf. Fig. 24, *a*) which have recently been formed by tangential division. The cells of the limiting layer always have dense contents and numerous brown chromatophores, so that the section needs to be particularly thin to show the cell structure without the use of clearing reagents.

b. Cortical Layers. — The next layers differ in stipe and in blade in the details. In the blade the cortical layer is not at all distinctly divided into inner and outer, as seen in cross-section. In a longitudinal section, however, the innermost cells are elongated and have hyphal outgrowths, while the outer ones are shorter and more irregularly placed. In the stipe the outer cortex appears distinct in a transverse section, from its cells being somewhat elongated radially and arranged in radial rows, although it is not as plain in this species as it is in those of the genus *Laminaria*. The cells of the inner cortex of the stipe appear more nearly hexagonal in transverse section, and are not

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* Obs. Phyc., Part. III. p. 12.

arranged in radial rows. In a longitudinal section of the stipe the cells of the outer cortex are short and more or less irregularly placed, while the cells of the inner cortex are much elongated and in vertical rows. In the blade there are only a couple of layers of cells in each cortex, but in the stipe there are several layers of cells in each, and the cells of the layers are well supplied with pits.

The pits among the *Laminariaceæ* are very conspicuous structures, and deserve especial study. They are mentioned and described by a number of writers on the subject, but no satisfactory account of their development has yet been published. They appear quite early in the second period of growth, but are not readily seen until reagents are applied. When the section, however, is treated with chloriodide of zinc solution, or dilute Boehmer's or Kleinenberg's hæmatoxylin, they appear as circular uncolored places, and are large in proportion to the size of the cells on the walls of which they occur. They are to be found for the most part on the walls of the cells of the inner cortex and medulla, but are present sparingly on the walls of the innermost layers of cells of the outer cortex. In the inner cortex of older specimens the cell walls are very much thickened. There is an appearance like the middle lamella of wood cells, and the walls themselves are plainly stratified. The pit appears to be situated in the stratified portion, and to consist of two opposite depressions in the adjacent walls of neighboring cells, which are separated at this point only by a very thin membrane. When treated with chloriodide of zinc or iodine followed by sulphuric acid, the inner linings of the cells turn rapidly blue, and after a time there is a faint blue coloration through the whole thickness between two cells. The whole thickness, too, stains deeply with hæmatoxylin.

c. Medulla. — The tubes (or long tubular cells) are a conspicuous feature in sections of the adult plant, both of blade and of stipe. As we have seen, they arise very early in the history of the plant. It is somewhat obscure as to just how the first tube arises. Probably a middle cell is cut off between the two layers, and has a chance to elongate before another one is formed; for, as we have seen, the tubes in the young plant were few and scattered. Later, however, new tubes are formed from the inner cells of the inner cortex, and come to lie with the old ones in the medulla. The walls of these tubular cells begin to thicken before those of the other cells, and are of considerable thickness even in the preceding period. These cells form a layer adjoining those of the inner cortex on either side in the blade, and in the stipe this layer appears in cross-section as an ellipse of occasionally as many as four to six cells in thickness. The very central mass, both of the medulla of the stipe and of the medulla of the blade, consists of densely interwoven hyphæ, which have made their way in from the surrounding cells, and have crowded the tubes out to the periphery.

In the very old stipes, and to a somewhat less degree in the blades, the tubes form an important factor in rendering them as tough and leathery as they are. When such fronds are macerated in potash, the limiting and cortical layers may be removed, and a firm mass of fibrous tissue left, which is in the form of a flat plate in the blade, while that from the stipe is a cylinder hollow or spongy in the middle. This layer is unbroken at the transition place, which shows that in the adult plants this region is no longer the seat of active growth.

It is easy to isolate individual fibres from macerated specimens to get a better idea of their shape and size. They have, without exception, a longitudinal course, very nearly vertical, and lie closely crowded with overlapping ends. They are for the most part simple, but some are slightly branched at one end.

In a macerated stipe 9.3 cm. long, the longest fibre (or thickened tubular cell) was 7.5 cm. long, and was terminated only at one end, the other being broken off short. A whole one obtained from the same stipe was 7.3 cm. long, and one of more average length was 6.2 cm. long. A very small one measured 3.2 cm. The fibres from the blade are much shorter, averaging from 3 to 4 cm. in length.

In Figure 25, *a*, *b*, *c*, are represented the tips of various fibres as seen in optical section. They are of various shapes, and frequently have spiny projections which are probably traces of the connecting hyphæ with which in their earlier stages they were united with adjacent cells. In June plants, they have a thickened and stratified wall and a wide lumen. The contents at this time also line the wall, and are dense and of a yellow color. But in the specimens figured, which are from an October plant, the lumen is almost obliterated. The walls are composed of very distinct layers. The treatment with potash and a prolonged soaking in water are responsible for some of this, but not for the greater portion. The walls when treated with chloriodide of zinc solution finally become a pale watery blue.

These fibres, both as regards shape and arrangement, remind one of the fibres in the bands of brown tissue so common in the stems and stipes of ferns which are called *sclerenchyma fibres.* There seems to be no reason why these structures should not be called by the same name.

Sclerenchyma fibres occur also in *Saccorhiza bulbosa*, as I have learned from the examination of specimens in Professor Farlow's herbarium, but they do not seem to be so regularly parallel as in *S. dermatodea*. They have never been studied by any one, so far as I know. Even the references to them are few. Janczewski * mentions "cellules très-longues à membrane épaissie simulant des fibres libériennes," in "*Haligenia*," referring of course to *Saccorhiza bulbosa*. Kjellman, as I have mentioned above, both describes and figures them for his *Phyllaria dermatodea*. He says that they are also present (i. e. "the long tubular cells") in *Phyllaria lorea*, "but their walls are always thin, not differing in thickness from the walls of the adjoining parenchymatous cells." †

d. Splitting. — The splitting of the frond, although fairly regular and uniform, yet seems to be of the nature of a wound. In some specimens this splitting does not occur at all, but the majority of plants split early. The blade widens, and, being exposed to the buffetings of the waves, naturally tends to split. On account of the structure of the fibrous masses of tissue, it splits readily in a longitudinal direction rather than transversely. If the splitting happens when the plant is still young and actively growing, the limiting and cortical layers continue to increase, while the medulla, having no growth of its own, is left behind. Consequently, there is soon a depression or channel formed on the wounded edge. Under favorable conditions the sloping sides of this channel continue to grow until they meet and fuse, and then sections show no trace of the wound. In old specimens, however, these outer layers are not growing, and so, when the split occurs in such a frond, the edges exposed simply thicken and harden, and a section always gives evidence of the wound. Almost all the stages between these two conditions are met with.

e. Fruit. — The last organs to be developed are the reproductive organs. This occurs at Nahant and Peak's Island in the autumn and winter. Specimens just beginning to develop sporangia were found at Nahant in the last part of September, and fruiting specimens are to be found from that time on until May.

The reproductive organs are borne on the surface of the blade in large patches known as "sori." They are of two kinds, zoosporangia

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* Mém. Soc. Nation. Sci. Nat. Cherbourg, Tom. XIX. p. 98 (p. 2 of reprint), 1875.

† Arct. Alg., pp. 224, 225.

and paraphyses. The September specimens show many details of the development. The cells of the limiting layer elongate perpendicularly to the surface of the frond until they are ten to twelve times as long as broad. These elongated cells are slightly swollen at the tips, and have granular brown contents and constitute the paraphyses. At maturity, each is cut off from the cell whence it arose by a tangential wall. The cuticula has been carried up and still covers the tips of the paraphyses. After they are fully formed, the zoosporangia begin to appear as small and broad swellings at the bases of the paraphyses. They generally arise from the basal cell of a paraphysis; at least, in all cases where the point of origin could be distinctly determined this was the case.

In November specimens, the zoosporangia are well developed. The cuticula has disappeared from over the tops of the paraphyses, and the sori in consequence have taken on their characteristic velvety appearance. The paraphyses themselves have a slightly thickened tip. The zoosporangia are in the shape of obovoid sacs, about two thirds the length of the paraphyses. The contents are of a light yellow brown and are already divided up into spheres, the future zoospores. The tip of the zoosporangium is noticeably thickened.

Farlow * has called attention to the fact that the paraphyses are destitute of the hyaline appendage of the paraphyses of the species of *Laminaria*. Areschoug † has given measurements of both zoosporangia and paraphyses. Kjellman ‡ figures a zoosporangium and a paraphysis; but these drawings do not correspond exactly to the zoosporangia and paraphyses of my specimens. Barber § has figured and described the zoosporangia and paraphyses of *Saccorhiza bulbosa*, which seem to agree very well with those of our plant.

GENERAL SUMMARY.

I. The development of *Saccorhiza dermatodea* agrees in its general features with what is known of the development of other *Laminarieæ*.

II. The permanent holdfast is developed from a peculiar organ, the rhizogen, which produces two successive whorls of hapteres, the first organ of attachment or primitive disk being only a temporary structure.

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* N. E. Alg., p. 96.

† Obs. Phyc., Part. III. p. 12.

‡ Spetsb. Thall., II., Taf. I. Fig. 8, 9, 1877.

§ Annals of Botany, Vol. III. p. 58, Pl. VI. Fig. 22.

III. The cryptostomata are present on the one-layered portion of the blade as clusters of hairs upon the flat surface; in the more complex portions, they occupy saucer- or bowl-shaped depressions; and these finally are provided with a prominent projecting margin, as shown above.

IV. The medulla is largely made up of hyphæ developed in the same way as in the other *Laminarieæ.*

V. Peculiar sclerenchyma fibres are developed in the medulla both of the stipe and of the blade.

VI. The paraphyses are destitute of the conspicuous terminal appendage present in almost all the other *Laminarieæ.*

VII. There is present a series of stages in which the maximum of growth is attained, and this series of stages is more or less sharply marked off from the adult stages by a process very similar to that known as "the renewing of the blade" in other *Laminarieæ.*

VIII. The adult frond is destitute of cryptostomata.

Relation to Phyllaria lorea, Kjellm. — Kjellman has made a careful study of the old *Laminaria lorea,* Bory,* and has decided that it is a distinct species, but high Arctic in its distribution. He has given his reasons for considering it distinct from the *Laminaria dermatodea,* De la Pyl., in the "Arctic Algæ." Strömfelt † follows Kjellman in keeping it distinct. I have searched for the species most carefully among my collections from the New England coast, and have studied Kjellman's descriptions in order that I might be able to recognize the plant. The following comparison between my experience with New England *Saccorhizæ* and Kjellman's with Spitzbergen and Norwegian specimens may throw some light on the subject.

Beginning with the young plants, Kjellman says that there is a marked difference between the two species. Young plants of *S. dermatodea* have a distinct stipe, a dark brown color, are "only little translucent, and provided with very few short-haired cryptostomata." The other species (*Ph. lorea*) has only a "very short stipe, passing without definite limit into a narrow, sometimes almost filiform, linear, or more usually lanceolate lamina. Their lamina is thin, very light brown, almost yellowish brown, perfectly pellucid with numerous long-haired cryptostomata." ‡

The great majority of the young *Saccorhizæ* to be found along the

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* In J. Ag., Spec. Alg., Vol. I. p. 130, 1848.

† Algveg. Isl., pp. 42 and 76, 1886.

‡ Arct. Alg., p. 224.

New England coast answer perfectly to this description of *Phyllaria lorea.* Only a very few were found which would at all agree with the description of *Ph. dermatodea*, and these few always seemed to be the product of unfavorable circumstances which had dwarfed them. The shapes too of the young specimens figured in the "Arctic Algæ" * agree very well with numerous specimens collected at Nahant. Kjellman further says, that "older specimens of the two species are easily distinguished from each other by several good characteristics. In *Ph. lorea* the stipe collapses in drying, and becomes flat, thin, almost membranaceous, and brittle; even in very large specimens, it has the same color as the lamina, being pellucid like this. In older specimens of *Ph. dermatodea* the stipe is far more solidly built, dark brown, opaque, flat upwards, but almost terete downwards."† Of my New England specimens, very large ones, in fact many of the very largest, answer almost exactly to this description of *Phyllaria lorea.* When dried, both stipe and blade become very thin and membranaceous, and extremely brittle. The stipe is light yellow-brown still in many cases, and the cryptostomata are very numerous and long-haired. In such specimens, too, the tubular cells are thin-walled, and with a very wide lumen. It is not until very late that these plants have cryptostomata with a prominent overhanging margin. They have all the characters, so far as I can see, that distinguish *Ph. lorea* from *Ph. dermatodea.* But these same specimens, as observed in tide pools at Nahant, soon begin to lose these characteristics. They become thicker and more solid both in stipe and in blade; they grow darker; they become shorter; the distinction between stipe and blade becomes more marked; — in fact, they come to have all the marks which serve to distinguish the *Phyllaria dermatodea* of Kjellman. Furthermore, all the plants of *Phyllaria lorea* taken by Kjellman were young. Only one was taken which had zoosporangia in course of development.‡

Professor Kjellman has very kindly sent me specimens both of his *Phyllaria lorea* and his *Ph. dermatodea.* The specimens of *Ph. lorea* agree exactly with my young specimens, which undoubtedly belong to *Saccorhiza dermatodea*, while the specimens of *Ph. dermatodea* correspond in all characters except size to older specimens of the same. Most of my browner specimens are larger, but, as the species is very variable in size, this does not seem to me to be of any great importance. I have little hesitation in believing that the *Laminaria lorea*, Bory,

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* Taf. XXIV. Figs. 1, 2.

† Arct. Alg., p. 224.

‡ *Loc. cit.*, p. 227.

and the *Phyllaria lorea*, Kjellm., are younger, and perhaps in certain cases more delicate, stages of *Saccorhiza dermatodea.*

In his recent paper on the Algæ of East Finmark (p. 74), Foslie describes some young stages of *Saccorhiza dermatodea* which seem to agree very closely with those occurring on the New England coast, and his remarks on these tend to confirm the views expressed above.

Forms of Saccorhiza dermatodea. — Kjellman * describes two forms of his *Phyllaria dermatodea,* one of which, f. *typica,* has abundant cryptostomata; and under this he makes a reference to Farlow's plant described in the New England Algæ. But, as I have shown, the adult plant has no cryptostomata, which character would tend to refer it to the other form, *arctica,* which has no cryptostomata in the adult condition. But f. *arctica* has few in the young condition, according to the description. Here, however, I may refer to what I have shown above, that Kjellman's description of the young *Ph. dermatodea* does not agree entirely with mine. As the Norwegian plant distributed by Areschoug agrees well with our New England specimens, it certainly seems to me that these two varieties or forms of Kjellman represent merely different stages in the life history of one plant.

In the paper on the Algæ of East Finmark alluded to above, Foslie describes two new forms of *Saccorhiza dermatodea* (p. 74). These, as nearly as can be judged from the description, exist also among New England specimens; but there is no constant difference, and they seem to me to be merely states of the same plant, differing in shape and color on account of difference in age, or with varying conditions of light, exposure, etc. F. *lanceolata,* as far as measurements and description indicate, is mostly a younger and more delicate form than f. *oblonga.* On the New England coast the matured fruiting plants are remarkably uniform in size, shape, and color for a species of the *Laminariaceæ,* and so I can see no reason for separating our plant at least into different varieties or forms.

Relation to Saccorhiza bulbosa, De la Pyl. — The resemblance between *S. bulbosa* and *S. dermatodea* is pointed out by De la Pylaie in his first paper.† The rhizogen and the production of the two whorls of hapteres are the same in both species. After that the rhizogen of *S. dermatodea* ceases to form hapteres, while that of *S. bulbosa* continues to do so indefinitely, and produces that characteristic organ, "the bulb." The development of the tissues in this organ is, so far as

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* Arct. Alg., p. 223.

† Ann. Sci. Nat., Ser. 1, Tom. IV. p. 179.

I can judge, essentially the same in the two species. *S. bulbosa*, too, is the only other alga, as far as is known, that possesses the peculiar sclerenchyma fibres. Furthermore, *S. bulbosa* has paraphyses of the same peculiar kind with *S. dermatodea*. Both are annual plants, while the majority of the *Laminarieæ* are perennials. These two species seem to constitute a distinct and natural genus, in which are also placed several smaller European species of more or less doubtful autonomy. *Saccorhiza*, proposed by De la Pylaie in 1829,* has the right of priority. *Haligenia*, proposed by Decaisne in 1842,† included *S. bulbosa* only. It was extended in 1856 by Le Jolis ‡ to include *S. dermatodea*. Le Jolis divided *Haligenia* into two sections: *Saccorhiza*, to include *S. bulbosa*, etc., and *Phyllaria*, to include *S. dermatodea* and others. *Phyllaria* has since been used by Gobi § and Kjellman ‖ as an independent genus. Kützing made *S. bulbosa* the type of the genus *Phycocastanum* in 1843.¶ There seems to be no need of separating the two species, and consequently they should both be included under the older name of *Saccorhiza*.

Relation to the other Laminarieæ. — The relation of these two species to the rest of the species of the *Laminarieæ* is at once complex and interesting. The first organ that suggests itself as important in this discussion is the holdfast. *Chorda* has in all probability the simplest holdfast of any member of the group. The holdfast in this genus appears to be merely the primitive disk expanded. Nothing like hapteres is produced. *Laminaria solidungula* seems to reproduce the holdfast of *Chorda*, but on a larger scale. Next comes *Saccorhiza dermatodea*, in which the primitive disk does not produce hapteres, and where only two successive whorls of hapteres are produced from the rhizogen. *Saccorhiza bulbosa* differs not only in producing a greater number of whorls of hapteres from the rhizogen, and the consequent enlargement of that organ, but also in producing hapteres from the primitive disk as well.**

In the rest of the *Laminarieæ* the holdfast is more complex. In most cases the hapteres are numerous and branched, and it seems a difficult task to bring them into homology with these simpler forms. But they may be separated into two classes: *first*, those with hapteres

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* Fl. Terre Neuve, p. 23.

† Ann. Sci. Nat., Ser. 2, Tom. XVII. p. 330.

‡ Examen I., p. 591.

§ Alg-Fl. Weiss. Meeres, p. 75, 1878.

‖ Arct. Alg., p. 223.

¶ Phyc. Gen., p. 346.

** Cf. Barber, Annals of Botany, Vol III. p. 46, Pl. V. Figs. 1, 2, 3, and 5.

in fairly distinct whorls; and *second,* those in which no arrangement into whorls can be traced.

Laminaria digitata, as limited by the Swedish algologists,* is a good example of the first of these. The primary disk here produces a few hapteres. The second set of hapteres is produced in a whorl, slightly above the region of the primitive disk. As all the hapteres of this whorl start out at about the same time, there is a bulging of the stipe in that region, giving it for a very limited period somewhat the appearance of a rhizogen; but it does not long continue, and at no time is there as definite a structure as the rhizogen of the *Saccorhizæ.* The hapteres push out very early, and a second whorl soon appears above the first, another above that, and so on. Although there is no real rhizogen present here, yet this whorled arrangement and the consequent bulging appear so very similar as to suggest that the two methods are very closely homologous.

Of the second class, the common *Alaria esculenta,* as now limited, is a good example. The primitive disk here produces hapteres, and the next hapteres above generally come out one by one, and apparently irregularly, although at times they seem to form a more or less regular whorl or two.

As far as the holdfast is concerned, then, *Chorda* is the simplest form. Between *Chorda* and *Saccorhiza bulbosa* we might expect to find a simple form with hapteres arising from the primitive disk, but we do not. The intermediate form is *Saccorhiza dermatodea,* with a simple primitive disk and a rhizogen of limited growth. In regard to the holdfast, too, *Saccorhiza dermatodea* seems directly related to *S. bulbosa,* on the one hand, and the digitate *Laminariæ,* on the other.

In structure, *Chorda* is perhaps the simplest: it has no trumpet hyphæ, and few ordinary hyphæ. The diaphragms, however, show a complication not present in other genera. *Saccorhiza* is of more complicated structure than *Chorda.* It lacks the trumpet hyphæ so characteristic of the other *Laminarieæ,* but possesses the peculiar sclerenchyma fibres in their stead.

The paraphyses of *Saccorhiza* are more like those of *Chorda* than those of the other *Laminarieæ,* being simpler in their structure.

Saccorhiza dermatodea, then, seems to be of simpler form and structure than any of the rest of the group except *Chorda.* It is Arctic in distribution, and circumpolar. This simplicity of structure and

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* Cf. Foslie, Die Lam. Norwegens, p. 60.

extended distribution seem to indicate that it is a primitive form, and more nearly related to the primitive ancestor of the *Laminarieæ* than any other known form except *Chorda*. *Chorda*, however, needs to be studied more carefully in order to determine its relationships more clearly.

LITERATURE.

Below are given as many of the references to *Saccorhiza dermatodea* as have come to the knowledge of the author: —

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Laminaria dermatodea, De la Pyl., Fl. Terre Neuve, pp. 48 to 52, 1829.

Laminaria Bærii, Post. & Rupr., Ill. Alg., p. ii, 1840 (nomen).*

Laminaria dermatodea, Rupr., Tange Och., pp. 352 and 409, 1847.†

Laminaria dermatodea, J. Ag., Spec. Alg., Vol. I. p. 131 (exclus. syn. *L. Bongardiana*), 1848.‡

Laminaria lorea, Bory, in J. Ag., Spec. Alg., Vol. I. p. 130, 1848.

Phyllitis dermatodea, Kütz., Spec. Alg., p. 567, 1849.

Laminaria dermatodea, Harvey, Ner. Am. Bor., pp. 91 and 92 (ex parte), 1852.§

Haligenia (*Phyllaria*) *dermatodea*, Le Jolis, Comptes Rendus, Tom. XL. p. 473, 1855.

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* Areschoug referred this name as a synonym under his *Laminaria lorea*, No. 213 of his "Algæ Scandinavicæ Exsiccatæ," by virtue of a specimen received from Ruprecht. He makes a further reference to it in the "Observationes Phycologicæ, Particula Tertia" (p. 12). Gobi places it under his *Phyllaria dermatodea* in "Die Algen Flora des Weissen Meeres" (p. 75), giving Rostafinski as his authority for doing so. Kjellman refers to Gobi as his authority for quoting this name as a synonym under the *Phyllaria dermatodea* of his "Algæ of the Arctic Sea" (pp. 223 and 225).

† Le Jolis in Examen II. puts under *Haligenia* (*Phyllaria*) *dermatodea*, "nec Rupr.," referring probably to this reference.

‡ Agardh quotes the *Laminaria Bongardiana*, Post. & Rupr., as a synonym of *Laminaria dermatodea*, De la Pyl., in the "Species Algarum," and has thus given grounds for the assertion (cf. Le Jolis, Examen I., p. 583) that the *L. dermatodea* of the "Species" was not the true *L. dermatodea*, De la Pyl. Agardh, however, in "De Laminarieis" (p. 33) explains how it was that he came to quote *L. Bongardiana* as a synonym of *L. dermatodea*, but asserts that nevertheless his reference really includes the true *L. dermatodea*, De la Pyl.

§ Harvey does not quote *L. Bongardiana*, Post. & Rupr., as a synonym; but his description of the old plants (for he says that he had seen only young specimens) was evidently taken from Agardh, and refers to some form of the true digitate *Laminariæ*.

Haligenia (Phyllaria) dermatodea, Le Jolis, Examen II., p. 312, 1855.*

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Laminaria dermatodea, Farlow, Proc. Am. Acad., Vol. II. p. 355, 1875.

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Phyllaria dermatodea, Gobi, Alg. Fl. Weiss. Meeres, p. 75, 1878.

Laminaria dermatodea, Robinson, Flora of Essex Co., p. 163, 1880.

Saccorhiza dermatodea, Farlow, N. E. Algæ, pp. 95 and 96, 1881.

Saccorhiza dermatodea, Collins, Torr. Bull., Vol. IX. p. 71, 1882.

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[*] Examen I. was presented to the Imperial Academy at Breslau in 1854, but was not published until 1856. Examen II. was published in the Memoirs of the Imperial Academy at Cherbourg in 1855. In the mean time a summary had appeared in the Comptes Rendus (Tom. XL. p. 470), and reviews in the Annals and Magazine of Natural History (2d Ser., Vol. XV. p. 318, April, 1855), and in the Regensburg Flora, as is mentioned in a note appended to Examen II.

[†] J. G. Agardh says, on page 18 of "De Laminarieis," that *L. dermatodea*, Harv., "in scedula," is his *Laminaria fissilis*, and adds, "sec. specim. distrib."

Phyllaria dermatodea, Kjellm., N. Ishafv. Algfl., pp. 278 to 282, Taf. 25, Figs. 1 to 4, 1883.

Phyllaria lorea, Kjellm., N. Ishafv. Algfl., pp. 282 and 283, Taf. 24, Figs. 1-3, Taf. 25, Figs. 5, 6, 1883.

Phyllaria dermatodea, Kjellm., Arct. Alg., pp. 223 to 225, Taf. 25, Figs. 1 to 4, 1883.

Phyllaria lorea, Kjellm., Arct. Alg., pp. 226 and 227, Taf. 24, Figs. 1 to 3, Taf. 25, Figs. 5, 6, 1883.

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Exsiccatæ.

Laminaria lorea, Aresch., Alg. Scand. Exss., No. 213.

Saccorhiza dermatodea, Farl., Eaton and Anders., Alg. Am. Bor. Exss., No. 120, 1879.

I desire to express my thanks to Prof. W. G. Farlow of Harvard University, in whose laboratory and under whose direction the present paper was prepared, for assistance at every point; also to Dr. G. H. Parker of Harvard University, and to Mr. F. S. Collins of Malden, Mass., for valuable aid in the way of materials.

CRYPTOGAMIC LABORATORY, HARVARD UNIVERSITY,
June 1, 1891.

EXPLANATION OF THE FIGURES.

Plate I.

Fig. 1. Diagram of a very young plant rather narrower than the typical form. The midrib-like portion is shaded. × 10.

Fig. 2. Diagram of a very young plant of the typical form. The midrib-like portion is shaded as in Fig. 1. × 10.

Fig. 3. Sketch of a young plant from Nahant, showing no trace of a rhizogen. A = the primitive disk; C = the stipe; D = the more complex blade; E = the primitive blade. × 1.75.

Fig. 4. Sketch of a young plant showing the rhizogen at B. Other letters as in Fig. 3 × 1.

Fig. 5. Sketch of a young plant in which the hapteres are just appearing. × 1.

Fig. 6. Sketch of a plant somewhat more advanced. × 1

Fig. 7 Sketch of the base of a young plant in which the hapteres (F) are well developed, but in which the primitive disk (A) still persists. × 1.

Fig. 8. Diagram showing the point of attachment of the primitive disk (1) and of each of the first set of hapteres (2). × 1.

Fig. 9. Sketch of the base of a young plant showing the primitive disk (A) still remaining, the first set of hapteres attached, and the second set of hapteres just appearing. × 1.

Fig. 10. Sketch of the base of a small adult plant collected at Nahant in February, 1890, showing the permanent holdfast, the flattened stipe, and the "oar-shaped" base of the blade. × 1.

Fig. 11. Tracing of the outline of the base of a young plant having the appearance of "renewing the blade." At A is the constriction between the young and the adult portions. × 1

Fig. 12. Diagram of a portion of a transverse section of the blade of a specimen 1.2 cm. long, showing at A and A the beginnings of the more complex portion. × 500.

Fig. 13. About 30 μ below the section represented in Fig. 12. × 500.

Fig. 14. Diagram of a portion of a transverse section still lower down on the same plant, showing the three-layered blade in the centre and the one-layered blade on the sides. In the very centre is shown the transverse section of a young sclerenchyma fibre, and at one side are the bunches of hairs belonging to young cryptostomata. × 500.

Fig. 15. Diagram of a little more than half of a transverse section below that represented in Fig. 14, showing the proportion existing between the three-layered blade of the centre and the one-layered blade at the sides. × 385.

Fig. 16. Diagram of a portion of a transverse section below that represented in Fig. 15. × 500.

Fig. 17. Diagram of a portion of a transverse section showing at B the origin of a second more complex portion of the blade. At A is the transverse section of a sclerenchyma fibre. × 385.

Fig. 18. About 15 μ below Fig. 17. *a*, *a*, represent transverse sections of young sclerenchyma fibres. × 385.

Fig. 19. Diagram of a portion of a transverse section still lower down. L, L = limiting layers; C, C = cortical layers. × 385.

Fig. 19 *a*. Diagram of a small portion of a similar section showing two young sclerenchyma fibres. × 385.

Fig. 20. Diagram of a portion of a longitudinal section in the same portion of the blade as that represented in Fig. 19, with the same lettering. The shaded band in the middle represents a young sclerenchyma fibre. × 385.

PLATE II.

Fig. 21. Diagram of a portion of the centre of a transverse section through a rhizogen which has produced one set of hapteres. *a*, sclerenchyma cells; *b*, hyphal cells. × 500.

Fig. 22. Diagram of a section through the centre of a young cryptostoma in the transition place of a frond about 20 cm. long. × 500.

Fig. 23. Diagram representing portions of two elongated cells of the inner cortex of a young specimen, showing the thickenings around the pits. × 500.

Fig. 24. Diagram of a small portion of the margin of a transverse section of the stipe of a specimen collected at Nahant in September, 1889. L = the limiting layer; *a* = a couple of cells which have recently divided off from the peripheral cell. × 500.

Fig. 25, *a*, *b*, *c*. Diagrams of tips of sclerenchyma fibres seen in median longitudinal optical section. From a specimen collected at Nahant in December, 1889. × 385.

XIV.

ON SOME SIMPLE CASES OF ELECTRIC FLOW IN FLAT CIRCULAR PLATES.

By B. O. Peirce.

Presented May 13, 1891.

1. It is well known * that, if in a thin conducting plate of indefinite extent there are two sources and a sink, each of strength numerically equal to m, situated respectively at points A, B, C, which lie in order upon a straight line, one of the lines of flow consists in part of a circumference of radius $\sqrt{CA \cdot CB}$ drawn around C as a centre; so that the flow inside the circumference would be unchanged if the part of the plate outside it were cut away. In other words, if a circumference be drawn in a thin conducting plane plate of indefinite extent, the "image" in this circumference of a source, of strength m, situated at a point P in the plane, is made up of a sink, of strength m, at the centre of the circle, and a source of the same strength at Q, the inverse point of P with respect to the circumference.

If a sink be regarded as a negative source, it follows from this that if inside a circumference drawn in a thin plane conducting plate of indefinite extent there are sources at the points $A_1, A_2, A_3, \ldots. A_k$, of strengths algebraically equal to $m_1, m_2, m_3, \ldots. m_k$, respectively, and sources of strengths algebraically equal to $-m_1, -m_2, -m_3, \ldots. -m_k$, at the corresponding inverse points, then, if $m_1 + m_2 + m_3 + \ldots. + m_k = 0$, there is no flow of electricity across the circumference.

2. If, at a fixed point P in a thin plane plate there is a sink of strength numerically equal to m, and at another point P' in the plate an equal source, and if P' be made to approach P as a limit and the product $m \cdot PP'$ be kept always equal to a given constant, μ, we have

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* Kirchhoff, Pogg. Ann. 1845, p. 497; W. R. Smith, Proc. Ed. Roy. Soc., 1869–70; Foster and Lodge, Phil. Mag., 1875; Minchin's "Uniplanar Kinematics," p. 213; etc., etc.

as a limit a "doublet"* of strength μ, the axis of which is PX, the limiting position of the straight line drawn *from P to P'*. We shall find it convenient to represent sources and sinks respectively by black and unshaded circles, and doublets by circles half black and half unshaded. The black portion of a doublet circle indicates the directions in which there is a flow *away from* the point where the doublet is situated; the unshaded portion indicates the directions from which there is a flow *towards* this point. The axis of a doublet bisects both the black and unshaded portions of the doublet circle. (See Fig. 1.) If P be used as origin and PX as axis of abscissas, the velocity potential function due to the doublet is $\phi = -\frac{\mu x}{x^2 + y^2}$ and the flow function is $\psi = \frac{\mu y}{x^2 + y^2}$. If $x + yi = z$, these are respectively the real part and the real factor of the imaginary part of the function $\frac{-\mu}{z}$.

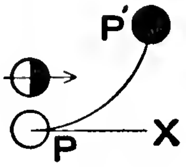

FIG. 1.

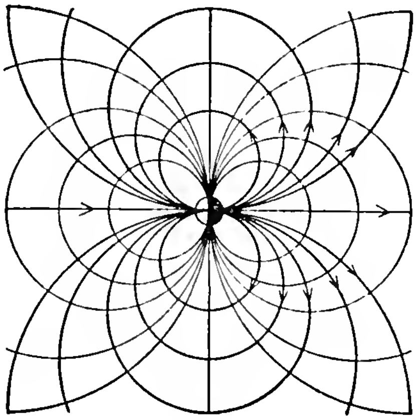

FIG. 2.

The equipotential lines and the lines of flow are circles (see Fig. 2) touching the axes of y and x respectively at the origin.

In uniplanar motion, the velocity at a point M due to a doublet of strength μ at a point P is numerically equal to $\frac{\mu}{\overline{PM}^2}$, and is directed

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* Basset, Treatise on Hydrodynamics, Art. 47; Mascart and Joubert, Treatise on Electricity and Magnetism, Art. 151; Neumann, Untersuchungen über das Logarithmische und Newton'sche Potential, Chap. IV.; etc., etc.

along a straight line MN such that PM bisects the angle between MN and the axis of the doublet. In all that follows, the motion will be assumed to be uniplanar.

3. If, in the subjoined figure, $\overline{OL} \cdot \overline{ON} = \overline{OL'} \cdot \overline{ON'} = \overline{OA}^2$, and if there are sources, of strength m, at L' and N', and equal sinks at L and N, there will be no flow across the circumference drawn around O with OA as radius. The value at P, the co-ordinates of which are x and y, of the flow function due to these sources and sinks is, if $OL = a$, $LL' = \delta$, $OA = r$,

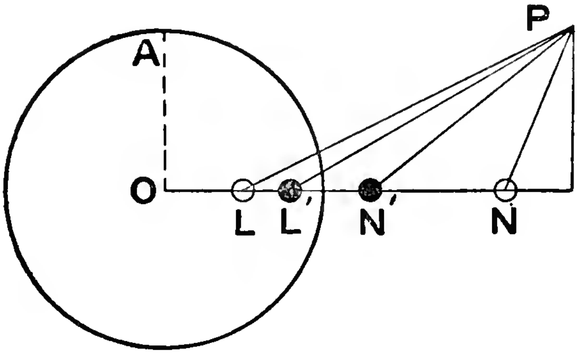

FIG. 3.

$$\psi_P = m\left\{\tan^{-1}\frac{y}{x-(a+\delta)} - \tan^{-1}\frac{y}{x-a} + \tan^{-1}\frac{y}{x-\dfrac{r^2}{a+\delta}} - \tan^{-1}\frac{y}{x-\dfrac{r^2}{a}}\right\}$$

$$= m\left\{\tan^{-1}\frac{\delta y}{(x-a)^2-\delta(x-a)+y^2} - \tan^{-1}\frac{r^2\delta y}{(ax-r^2)^2+\delta x(ax-r^2)+a(a+\delta)y^2}\right\}.$$

If now δ be made to approach zero as a limit, and m to increase in such a way that $m \cdot \delta$ is always equal to a constant, μ, the circumference just mentioned continues to be a stream line and the flow function due to the combination of a doublet of strength μ at L with axis coincident with the radius drawn through L, and the image of this doublet in the circumference is

$$\underset{\delta \doteq 0}{\text{Limit}}\ \psi_P = \mu\left\{\frac{y}{(x-a)^2+y^2} - \frac{r^2}{a^2} \cdot \frac{y}{\left(x-\dfrac{r^2}{a}\right)^2+y^2}\right\}. \qquad (1)$$

It is evident from this result (see section 2) that the image of a doublet of strength μ so situated at a point L — which is at a distance a from the centre of a circumference drawn with radius r on a thin plane indefinitely extended plate — that its axis coincides with the radius drawn through L, is a doublet of strength* $\mu \frac{r^2}{a^2}$ and axis making an angle of 180° with that of the first, at the inverse point of L with respect to the circumference.

It is to be noticed that the flow function given by (1) is the real factor of the imaginary part of the function

$$w = - \mu \left\{ \frac{1}{z - a} - \frac{r^2}{a^2} \cdot \frac{1}{z - \frac{r^2}{a}} \right\}.$$

4. By differentiating (1) partially with respect to y and $-x$, respectively, we get the velocity components at the point (x, y) corresponding to the case which we have been considering. They are

$$u = D_y \psi = \mu \left\{ \frac{(x - a)^2 - y^2}{[(x-a)^2 + y^2]^2} - \frac{r^2}{a^2} \cdot \frac{\left(x - \frac{r^2}{a}\right)^2 - y^2}{\left[\left(x - \frac{r^2}{a}\right)^2 + y^2\right]^2} \right\}; \qquad (2)$$

$$v = - D_x \psi = 2 \mu y \left\{ \frac{x - a}{[(x-a)^2 + y^2]^2} - \frac{r^2 (a x - r^2)}{a^3 \left[\left(x - \frac{r^2}{a}\right)^2 + y^2\right]^2} \right\}. \qquad (3)$$

If we make a approach zero in order to obtain the flow in a thin circular plate due to a doublet at the centre, ψ as given by (1) grows larger without limit, but u and v approach the definite limits

$$u_0 = \mu \left\{ \frac{x^2 - y^2}{[x^2 + y^2]^2} - \frac{1}{r^2} \right\}, \qquad (4)$$

$$v_0 = \frac{2 \mu x y}{[x^2 + r^2]^2}; \qquad (5)$$

and these expressions solve the problem.

This case may be treated in another way, however. In Figure 4 let $OL = OL' = \delta$ and $OM \cdot OL = OL' \,.\, OM' = \overline{OA}^2 = r^2$; then, if there are sources of strength m at L and M and equal sinks at L' and M', one of the lines of flow due to this combination will consist in part of the circumference of radius r drawn about O as centre.

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* This does not agree with the statement made in the first edition of Basset's Treatise on Hydrodynamics, p. 56, where there seems to be a typographical error.

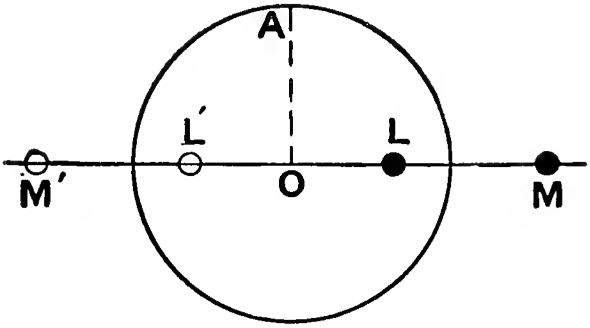

FIG. 4.

The value at the point (x, y) of the flow function is

$$\psi = m \left\{ \tan^{-1} \frac{y}{x - \delta} + \tan^{-1} \frac{y}{x - \frac{r^2}{\delta}} - \tan^{-1} \frac{y}{x + \delta} - \tan^{-1} \frac{y}{x + \frac{r^2}{\delta}} \right\}$$

$$= m \left\{ \tan^{-1} \frac{2\,\delta\, y}{x^2 + y^2 - \delta^2} + \tan^{-1} \frac{2\, r^2\, \delta\, y}{\delta^2 (x^2 + y^2) - r^4} \right\}.$$

If, now, δ be made to approach zero as a limit, and m to increase in such a way that $2\, m\, \delta$ is equal to the constant μ,

$$\psi_0 = \underset{\delta = 0}{\text{Limit}}\ \psi = -\frac{\mu\, y}{r^2} \left(\frac{x^2 + y^2 - r^2}{x^2 + y^2} \right); \qquad (6)$$

an expression which is equal to zero at every point of the circumference, $x^2 + y^2 = r^2$.

The velocity components u_0, v_0, obtained by differentiating (6), are identical with those given by equations (4) and (5).

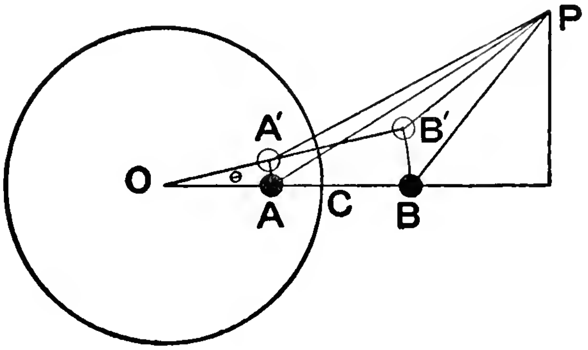

FIG. 5.

5. In Figure 5 let $OA = OA' = a$, $OB = OB' = b$, and $OA \cdot OB = OA' \cdot OB' = \overline{OC}^2 = r^2$, and let there be at A and B sources of strength m, and at A' and B' sinks of equal strength m; then one of the lines of flow due to this combination of sources and sinks in an

indefinitely extended plate will consist in part of the circumference of which OC is a radius. This shall be called the circumference C.

The value, at P, the co-ordinates of which are x and y, of the flow function is

$$\psi_P = -m\left\{\tan^{-1}\frac{y-a\sin\theta}{x-a\cos\theta} + \tan^{-1}\frac{y-b\sin\theta}{x-b\cos\theta} - \tan^{-1}\frac{y}{x-a} - \tan^{-1}\frac{y}{x-b}\right\}$$

$$= -m\left\{\tan^{-1}\frac{(x-a)(y-a\sin\theta)-y(x-a\cos\theta)}{(x-a)(x-a\cos\theta)+y(y-a\sin\theta)}\right.$$

$$\left. + \tan^{-1}\frac{(x-b)(y-b\sin\theta)-y(x-b\cos\theta)}{(x-b)(x-b\cos\theta)+y(y-b\sin\theta)}\right\}.$$

If now we let θ approach zero as a limit and m increase in such a way that the product of m and the straight line AA' shall always be equal to the constant μ, we have

$$\psi_0 = \underset{\theta \doteq 0}{\text{Limit}}\ \psi = +\mu\left\{\frac{x-a}{(x-a)^2+y^2} + \frac{r^2}{a^2}\cdot\frac{x-\frac{r^2}{a}}{\left(x-\frac{r^2}{a}\right)^2+y^2}\right\}, \quad (7)$$

the real part of the function

$$w = +\mu\left\{\frac{1}{z-a} + \frac{r^2}{a^2}\cdot\frac{1}{z-\frac{r^2}{a}}\right\}.$$

At every point of C, ψ_0 has the value $-\frac{\mu}{a}$.

The velocity components at P corresponding to ψ_0 are

$$u = -2\mu y\left\{\frac{x-a}{[(x-a)^2+y^2]^2} + \frac{r^2}{a^2}\cdot\frac{x-\frac{r^2}{a}}{\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]^2}\right\}; \quad (8)$$

$$v = +\mu\left\{\frac{(x-a)^2-y^2}{[(x-a)^2+y^2]^2} + \frac{r^2}{a^2}\cdot\frac{\left(x-\frac{r^2}{a}\right)^2-y^2}{\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]^2}\right\}. \quad (9)$$

If a is made to approach zero as a limit, these expressions approach respectively the limits

$$u_0 = \frac{-2\mu x y}{[x^2+y^2]^2}; \quad (10)$$

$$v_0 = \mu\left(\frac{x^2-y^2}{[x^2+y^2]^2} + \frac{1}{r^2}\right). \quad (11)$$

which agree with the expressions (4) and (5) obtained by using different co-ordinate axes.

We infer from (7) that the image of a doublet of strength μ so situated at a point A — which is at a distance a from the centre of a circumference drawn with radius r on a thin plane indefinitely extended plate — that its axis is perpendicular to the radius vector drawn through A, is a doublet, of strength $\mu \frac{r^2}{a^2}$ and axis parallel to that of the first doublet, at the inverse point of A with respect to the circumference.

If we make a equal to r, (7), (8), and (9) give us the flow function and the velocity components inside a circular plate when there is a doublet at some point of the circumference with its axis coincident with the tangent to the plate at the given point. The forms of these expressions might have been inferred from the results given in section 2.

6. It is to be noticed that if in Figure 6 $O'B'$ and OB are parallel lines, and OO', AA', and BB' perpendicular to them, and if there are sources of strength m at O', A, and B, and sinks of equal strength m at O, A', and B', a circumference drawn around O as centre with radius $\sqrt{OA\,.\,OB}$ will form part of a line of flow due to the combination of the sink at O and the sources at A and B, but not one of the lines of flow due to the combination of three doublets obtained by making $O'B'$ approach OB and increasing m at the same time so that $m\,.\,\overline{OO'}$ shall always be equal to the constant μ.

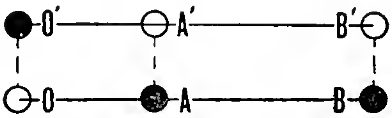

Fig. 6.

7. In Figure 7 let $OA\,.\,OB = OA'\,.\,OB' = OC^2 = r^2$, and $OA = a$, and let the curve AA' make with OM the angle δ. If, then, there are sources of strength m at A' and B', and sinks of strength m at A and B, one of the lines of flow will consist in part of the circumference (C) drawn with radius r about O as centre. If ψ_P is the value at P of the flow function due to this combination, the limit approached by ψ_P as A' is made to approach A along the curve $A'A$, and B' to approach B along the corresponding reciprocal curve $B'B$, will be the value at P of the flow function due to a doublet at A, the axis of which makes the angle δ with the radius drawn through A of the circumference C, and to the image of the doublet in C.

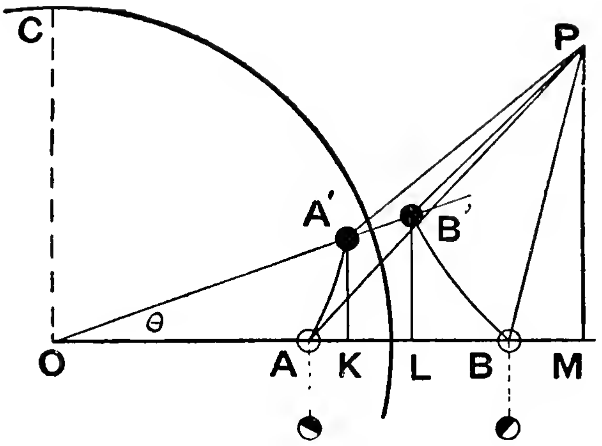

FIG 7.

$$\psi_P = m\left\{\tan^{-1}\frac{y-\overline{KA'}}{x-a-\overline{AK}} - \tan^{-1}\frac{y}{x-a} + \tan^{-1}\frac{y-\overline{LB'}}{x-OB-\overline{BL}} - \tan^{-1}\frac{y}{x-OB}\right\}$$

$$= m\left\{\tan^{-1}\frac{y\,.\,\overline{AK} - \overline{KA'}\,(x-a)}{(x-a)^2 + y^2 - y\,.\,\overline{KA'} - \overline{AK}\,(x-a)}\right.$$

$$\left.+ \tan^{-1}\frac{y\,.\,\overline{BL} - \overline{LB'}\,(x-OB)}{(x-OB)^2 + y^2 - y\,.\,\overline{LB'} - \overline{BL}\,(x-OB)}\right\}.$$

If A' be made to approach A as a limit, we have

$$\text{Limit}\ \frac{\overline{BB'}}{\overline{AA'}} = \frac{r^2}{\overline{OA}^2};\ \text{Limit}\ \frac{\overline{KA'}}{\overline{AA'}} = \sin\delta = \text{Limit}\ \frac{\overline{LB'}}{\overline{BB'}};$$

$$\text{Limit}\ \frac{\overline{AK}}{\overline{AA'}} = \cos\delta = \text{Limit}\ \frac{\overline{LB}}{\overline{BB'}};$$

and, if m be made to change so that $m\,.\,\overline{AA'}$ shall always be equal to the constant μ, Limit $(m\,.\,BB')$ will be equal to the constant, $\frac{r^2}{a^2}\,.\,\mu$.

$$\underset{AA'=0}{\text{Limit}}\ \psi_P = \psi_0 = \mu\left[\underset{\overline{AA'}\doteq 0}{\text{Limit}}\left\{\frac{\tan^{-1}\dfrac{y\,.\,\overline{AK} - \overline{KA'}\,(x-a)}{(x-a)^2+y^2-y\,.\,\overline{KA'}-\overline{AK}(x-a)}}{AA'}\right\}\right.$$

$$\left.+\frac{r^2}{a^2}\underset{\overline{BB'}\doteq 0}{\text{Limit}}\left\{\frac{\tan^{-1}\dfrac{y\,.\,\overline{BL} - \overline{LB'}\,(x-\overline{OB})}{(x-OB)^2+y^2-y\,.\,\overline{LB'}-\overline{BL}(x-\overline{OB})}}{\overline{BB'}}\right\}\right].$$

$$\psi_0 = \mu \,.\, \underset{\overline{AA'} \doteq 0}{\text{Limit}} \left\{ \frac{y \,.\, \dfrac{\overline{AK}}{\overline{AA'}} - \dfrac{\overline{KA'}}{\overline{AA'}}(x-a)}{(x-a)^2 + y^2 - y \,.\, KA' - \overline{AK}(x-a)} \right\}$$

$$+ \frac{\mu\, r^2}{a^2} \underset{\overline{BB'} \doteq 0}{\text{Limit}} \left\{ \frac{y \,.\, \dfrac{\overline{BL}}{BB'} - \dfrac{\overline{LB'}}{\overline{BB'}}(x-\overline{OB})}{(x-\overline{OB})^2 + y^2 - y \,.\, LB' - BL(x-\overline{OB})} \right\}$$

$$= \mu \left\{ \frac{y \,.\, \cos\delta - (x-a)\sin\delta}{(x-a)^2+y^2} - \frac{r^2}{a^2} \,.\, \frac{y \,.\, \cos\delta + \left(x - \dfrac{r^2}{a}\right)\sin\delta}{\left(x-\dfrac{r^2}{a}\right)^2 + y^2} \right\}. \qquad (12)$$

It follows from (12) that the image of a doublet of strength μ so situated at a point A — which is at a distance a from the centre, O, of a circumference drawn with radius r on a thin, plane, indefinitely extended plate — that its axis makes the angle δ with the radius drawn through A, is a doublet of strength $\frac{\mu\, r^2}{a^2}$ and axis making an angle of 180° — δ with the line OA, at the inverse point of A with respect to the circumference.

8. It was long ago noticed * that the functions

$$\log z, \; \frac{1}{z}, \; -\frac{1}{z^2}, \; \frac{2}{z^3}, \; -\frac{6}{z^4}, \; \ldots\ldots,$$

each of which is the derivative with respect to z of the one which precedes it, yield a series of pairs of conjugate functions which represent in order the velocity potential functions and the flow functions due to a source at the origin, to a doublet at the origin, to a quadruplet † at the origin, to an octuplet at the origin, and so on.

I will use the word *motor* to denote in general a source, a sink, a doublet, a quadruplet, or any other combination of sources or sinks at a single point. The strengths of two motors of the same kind shall be in the ratio of p to q if, when they are similarly placed at the same point successively, they give rise to velocity potential functions and flow functions which have values in the ratio of p to q at

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* See, for instance, Klein's Lectures on the Potential, or his paper, "Ueber Riemann's Theorie der Algebraischen Functionen und ihrer Integrale."

† A quadruplet is formed of two equal and opposite doublets in the same manner that a doublet is formed out of a source and an equal sink. An octuplet is formed in a similar way of two equal and opposite quadruplets, and so on.

every point. The unit motor of any kind and the direction of its axis, if it has any, may be chosen at pleasure.

Let there be in a plane any distribution, A, of n motors, either all of the same kind or of different kinds, of strengths respectively equal to $m_1, m_2, m_3, \ldots . m_n$.

Let there be also a system, B, of n motors, each respectively equal but opposite to a corresponding motor of A, and so situated in the plane that every motor of A could be superposed upon its equivalent in B by moving A parallel to itself through a distance δ in a direction making an angle α with the axis of x.

Let $u = f(x, y)$ and $v = \chi(x, y)$ be the values at the point (x, y) of the velocity components due to the system A, and let $\phi(x, y)$ and $\psi(x, y)$ be the corresponding values of the velocity potential function and the flow function.

It is evident that the velocity components due to B have values at (x, y) equal but opposite to those at the point $(x - \delta \cos \alpha,\ y - \delta \sin \alpha)$ of the corresponding velocity components due to A. We may, therefore, take for the values at any point (x, y) of the velocity potential and flow functions due to A and B existing together, the expressions

$$\phi(x, y) - \phi(x - \delta \cos \alpha,\ y - \delta \sin \alpha)\,; \tag{13}$$

$$\psi(x, y) - \psi(x - \delta \cos \alpha,\ y - \delta \sin \alpha). \tag{14}$$

If now B be made to approach A, by decreasing δ and keeping α constant, and if the strength of each of A's motors be made to grow so as to keep the product of itself and δ constant, the expressions just given approach as limits the velocity potential function and the flow function which A would yield if every one of its motors were *doubled up* with an equal but opposite motor approaching it from a direction which makes an angle α with the axis of x.

If $m_1 \delta = \mu_1$, $m_2 \delta = \mu_2$, $m_3 \delta = \mu_3$, etc., where the μ's are constant, the limits of the expressions (13) and (14) are the values obtained by changing every m into its corresponding μ in

$$\underset{\delta \doteq 0}{\text{Limit}} \left(\frac{\Delta_x \phi + \Delta_y \phi}{\delta}\right) \text{ and } \underset{\delta = 0}{\text{Limit}} \left(\frac{\Delta_x \psi + \Delta_y \psi}{\delta}\right)\,;$$

that is, in

$$\cos \alpha \,.\, D_x \phi + \sin \alpha \,.\, D_y \phi, \tag{15}$$

and

$$\cos \alpha \,.\, D_x \psi + \sin \alpha \,.\, D_y \psi. \tag{16}$$

If $w = f(z) = \phi(x, y) + i \,.\, \psi(x, y)$, the function of z which corresponds to the new velocity potential function and flow function may be found by changing every m into its corresponding μ in

$$-(\cos \alpha + i \,.\, \sin \alpha) \,.\, D_z w. \tag{17}$$

9. The equation $\frac{\sin n\,\theta}{r^n} = c$ represents a family of closed curves each of which is made up of $2\,n$ equal mutually distinct loops symmetrically situated about the origin; each curve passes n times through the origin and each loop is tangent there to two straight lines which include an angle of $\frac{\pi}{n}$. The equation $\frac{\cos n\,\theta}{r^n} = c$ represents the same family of curves turned around the origin through an angle $\frac{\pi}{2\,n}$.

The motor which gives rise to the flow function $\frac{\lambda \sin 2\,\theta}{r^2}$ may be denoted by the symbol shown in the upper part of Figure 8, in which the black portions show the directions in which fluid flows out from the point at which the motor is situated, and the open portions the directions from which fluid flows towards this point. The motor which corresponds to the flow function $\frac{\lambda \sin n\,\theta}{r^n}$ may be represented similarly by a circle drawn about the origin, and properly divided into n shaded and n unshaded sectors.

Let the motor A, which corresponds to the flow function $\psi_A = \frac{\sin n\,\theta}{r^n}$, be doubled up with an equal opposite motor which approaches it from a direction making an angle α with the axis of x. The flow function ψ_B, due to the resulting motor B, is given, apart from a constant factor, by the equation

$$\begin{aligned} \psi_B &= D_x\,\psi_A \,.\, \cos \alpha + D_y\,\psi_A \,.\, \sin \alpha \\ &= D_r\,\psi_A \,.\, \cos\,(\theta - \alpha) - \frac{D_\theta\,\psi_A}{r} \,.\, \sin\,(\theta - \alpha) \\ &= - \frac{n \,.\, \sin\,[(n+1)\,\theta - \alpha]}{r^{n+1}}\,. \end{aligned} \tag{18}$$

Referred to a new initial line drawn in a direction making an angle $\frac{\alpha}{n+1}$ with the old, this is

$$\psi_B = \frac{n \,.\, \sin\,(n+1)\,\theta}{r^{n+1}}\,; \tag{19}$$

and it is evident that the orientation of B's axis, but not B's character, depends upon α.

For instance, the flow function due to a unit doublet at the origin with axis coincident with the axis of x is

$$\psi_A = \frac{\mu\,y}{x^2 + y^2}\,.$$

If this motor be doubled up with its negative approaching from the positive part of the axis of x, the resultant quadruplet (see Fig. 8) corresponds to the flow function

$$\psi_B = \frac{-2xy}{(x^2+y^2)^2}.$$

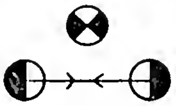

Fig. 8.

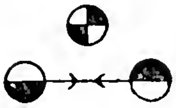

Fig. 9.

If, on the other hand, it be doubled up with an equal opposite doublet (see Fig. 9) approaching it from the positive part of the axis of y, the resultant quadruplet corresponds to the flow function

$$\psi_B = \frac{x^2-y^2}{(x^2+y^2)^2}.$$

One of these quadruplets is evidently equivalent to the other turned through an angle of 45°.

10. Besides the simple quadruplets obtained by combining two equal and opposite doublets just as a doublet is formed from a source and a sink, other combinations of two doublets sometimes appear when one attempts to find the image of a simple motor in the circumference of a circle in its plane.

In one common case, a fixed doublet D_1 of strength μ is approached by another doublet D_2, the axis of which remains always parallel but opposite in direction to that of D_1. The path of D_2 is a straight line, but its strength is equal to $\mu f(\delta)$, where δ is the distance between the two doublets at any time, and $f(\delta)$ is a finite, continuous, and single-valued function such that $f(0) = 1$. The product of μ and δ is kept always equal to a constant, λ.

The flow function due to a doublet of strength μ at the origin with axis coincident with the axis of x is $\frac{\mu y}{x^2+y^2}$, and the flow function due to a reversed doublet of strength $\mu f(\delta)$ at the point $(x - \delta \,.\cos \alpha,\; y - \delta \,.\sin \alpha)$

is
$$\frac{-\mu \,.\,(y-\delta \sin \alpha)\,.\,f(\delta)}{(x-\delta \,.\cos \alpha)^2 + (y - \delta \,.\sin \alpha)^2}.$$

The flow function due to the two doublets existing together is

$$\frac{\lambda}{\delta}\left\{\frac{y}{x^2+y^2} - \frac{(y-\delta \,.\sin \alpha)\,f(\delta)}{(x-\delta \,.\cos \alpha)^2 + (y-\delta \,.\sin \alpha)^2}\right\},$$

and the limit of this as δ approaches zero is

$$\frac{\lambda\,\{(x^2 - y^2)\,\sin\alpha - 2\,x\,y\,\cos\alpha - y\,(x^2 + y^2)\,f'(0)\}}{(x^2 + y^2)^2}; \qquad (20)$$

and this is equivalent to a simple quadruplet superposed upon a doublet of strength $-\lambda\,.\,f'(0)$ at the origin.

In general, let $\mu\,.\,\psi(x, y)$ be the flow function due to a fixed motor of strength μ, and of any kind; and let this motor be approached (keeping $\mu\,\delta$ constantly equal to λ) by an opposite motor of strength $\mu\,.\,f(\delta)$ from a direction making an angle α with the axis of x. The value at the point (x, y) of the flow function due to this second motor is the same as the value at the point $(x - \delta\,.\,\cos\alpha,\ y - \delta\,.\,\sin\alpha)$ of the flow function due to the first motor, so that the flow function due to the two motors existing together is

$$\frac{\lambda}{\delta}\,[\psi(x, y) - f(\delta)\,.\,\psi(x - \delta\cos\alpha,\ y - \delta\sin\alpha)],$$

and the limit approached by this as δ approaches zero is

$$\lambda\,[D_x\psi\,.\,\cos\alpha + D_y\psi\,.\,\sin\alpha - \psi(x, y)\,.\,f'(0)]. \qquad (21)$$

11. Let there be two equal opposite motors of the same kind at the points A and B in a plane equally distant from an origin, O, and let the axis of the motor at A make with the straight line OA the same angle that the axis of the motor at B would make with OB if its flow function were the negative of what it really is. If now OB be rotated about O so as to approach OA as a limit, and if the product of the strength of one of the motors by its distance from the other be kept equal to a constant, λ, we get as a limit a kind of motor which sometimes appears in practical problems.

Let $\mu\,.\,R(r, \theta)$ and $\mu\,.\,\Theta(r, \theta)$ be the values at the point P, the co-ordinates of which are r and θ, of the velocity components due to the motor at A, taken respectively parallel and perpendicular to the radius vector, OP. If the angle AOB (see Fig. 10) be α, the values of the velocity components at P due to the motor at B are equal but opposite in sign to values at the point P', the co-ordinates of which are r and $\theta - \alpha$, of the velocity components due to the motor at A. Hence the motors at A and B together cause at P the velocity components

$$\mu\,.\,R(r, \theta) - \mu\,.\,R(r, \theta - \alpha),$$

$$\mu\,.\,\Theta(r, \theta) - \mu\,.\,\Theta(r, \theta - \alpha).$$

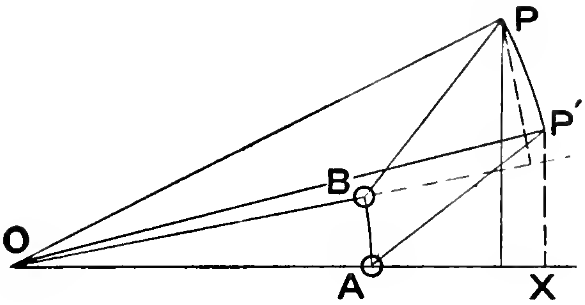

FIG. 10.

The limits of these expressions as a is made to approach zero, while $\mu \cdot a \cdot \overline{OA} = \lambda$, are

$$\frac{\lambda \cdot D_\theta\, R}{\overline{OA}} \text{ and } \frac{\lambda \cdot D_\theta\, \Theta}{\overline{OA}};$$

so that the flow function due to the newly found motor is obtained by changing μ to λ in the product of the reciprocal of $\overline{OA}$ and the derivative with respect to θ of the flow function due to the original motor at A alone; that is, in

$$\frac{x \cdot D_y\, \psi - y \cdot D_x\, \psi}{\overline{OA}}, \tag{22}$$

where $$\mu\, R = \frac{D_\theta\, \psi}{r} \text{ and } \mu\, \Theta = -\, D_r\, \psi.$$

A single doublet on the axis of x, at a distance a from the origin, with its axis perpendicular to the axis of x, yields, when combined with another similar motor in the way described in this section, the flow function

$$\psi = \frac{\lambda\, y\, (x^2 + y^2 - a^2)}{a\, [(x - a)^2 + y^2]^2}. \tag{23}$$

This is equal to zero on the axis of x and on the circumference of the circle drawn with the origin as centre so as to pass through the motor. It gives, therefore, a case of flow in a semicircular disk.

The flow function just found is the real factor of the imaginary part of the function

$$w = -\, \frac{\lambda\, z}{a\, (z - a)^2} = -\, \frac{\lambda}{a} \left\{ \frac{1}{z - a} + \frac{a}{(z - a)^2} \right\}. \tag{24}$$

The motor which corresponds to this flow function may be looked upon, therefore, as formed by superposing a doublet upon a quadruplet.

The image of such a motor (M) as this in a circumference drawn in its own plane with O as centre is a motor of the same kind as M, but of strength $\frac{r^2}{a^2}$ times as great as M's strength, situated at the inverse point with respect to the circumference of the point where M lies.

The flow function in this case is easily found, by a method analogous to that used in Section 5, to be

$$\frac{\lambda y}{a}\left\{\frac{x^2+y^2-a^2}{[(x-a^2)+y^2]^2}+\frac{r^2}{a^2}\cdot\frac{x^2+y^2-\frac{r^4}{a^2}}{\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]^2}\right\}. \tag{25}$$

The combination in the same manner of two pairs of motors of the kind just mentioned yields still another case of flow inside a circular disk due to a certain motor at a point Q, the co-ordinates of which are a and 0, and another motor at the inverse point of Q with reference to the circumference. The flow function in this case is

$$\psi=\frac{\lambda}{a^2}\left[\frac{x^2+y^2-a^2}{[(x-a)^2+y^2]^3}\left\{x(x-a)^2+y^2(x-4a)\right\}\right.$$
$$\left.+\frac{r^2}{a^2}\cdot\frac{x^2+y^2-\frac{r^4}{a^2}}{\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]^3}\left\{x\left(x-\frac{r^2}{a}\right)^2+y^2\left(x-\frac{4r^2}{a}\right)\right\}\right], \tag{26}$$

and this process might be carried on indefinitely.

12. The image of a simple quadruplet in the circumference of a circle drawn in its own plane is not another simple quadruplet, but a more complex motor.

On a straight line which passes through the centre of a circumference of radius r drawn in a plane, and which is taken for axis of x, let there be two equal and opposite doublets of strength μ with axis coincident with the line, at points distant respectively a and $a + \Delta a$ from the centre of the circumference. Let there be also on this line the two images of these doublets with respect to the circumference.

The value at the point (x, y) of the flow function due to these four doublets is

$$\mu y\left\{\frac{1}{(x-a)^2+y^2}-\frac{1}{(x-a-\Delta a)^2+y^2}+\right.$$
$$\left.\frac{r^2}{(a+\Delta a^2)\left[\left(x-\frac{r^2}{a+\Delta a}\right)^2+y^2\right]}-\frac{r^2}{a^2\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]}\right\};$$

and if Δa be made to approach zero, and μ to increase so that $\mu \,.\, \Delta a$ always has the constant value λ, this function approaches as its limit

$$\lambda\, y \left\{ \frac{2\,(a - x)}{[(x - a)^2 + y^2]^2} + \frac{r^2}{a^4}\; \frac{2\, r^2\, x - 2\, a\, (x^2 + y^2)}{\left[\left(x - \frac{r^2}{a}\right)^2 + y^2\right]^2} \right\}. \qquad (27)$$

If the axis of a simple quadruplet be a diameter drawn through the centre of the shaded portions of the symbol which represents the motor, the expression just found gives, with proper algebraic sign, the flow function due to a simple quadruplet in a circular disk with axis parallel or perpendicular to the radius drawn through the point at which the motor is situated.

The flow function, which vanishes at every point on the circumference, is the real factor of the imaginary part of the function

$$w = -\lambda \left\{ \frac{1}{(z - a)^2} + \frac{r^2}{a^4} \cdot \frac{r^2 - 2\, a\, z}{\left(z - \frac{r^2}{a}\right)^2} \right\}$$

$$= -\lambda \left\{ \frac{1}{(z - a)^2} - \frac{r^4}{a^4} \cdot \frac{1}{\left(z - \frac{r^2}{a}\right)^2} - \frac{2\, r^2}{a^3} \cdot \frac{1}{z - \frac{r^2}{a}} \right\}. \qquad (28)$$

The image of the simple quadruplet in question is made up, therefore, of a simple quadruplet and a doublet existing together at the inverse point, with respect to the circumference, of the point where the original quadruplet is situated.

13. If the axes of the doublets mentioned in the last section had been perpendicular to the axis of x instead of coincident with it, the flow function due to the four doublets would have been

$$\mu \left\{ \frac{x - a}{(x - a)^2 + y^2} - \frac{x - a - \Delta a}{(x - a - \Delta a)^2 + y^2} \right.$$

$$\left. + \frac{r^2}{a^2} \cdot \frac{x - \frac{r^2}{a}}{\left(x - \frac{r^2}{a}\right)^2 + y^2} - \frac{r^2}{(a + \Delta a)^2} \cdot \frac{x - \frac{r^2}{a + \Delta a}}{\left(x - \frac{r^2}{a + \Delta a}\right)^2 + y^2} \right\}.$$

The limit of this, as Δa aproaches zero and $\mu\, \Delta a$ is kept equal to the constant λ, is

$$+\lambda\left\{\frac{y^2-(x-a)^2}{[(x-a)^2+y^2]^2}-\frac{r^4}{a^4}\cdot\frac{1}{\left(x-\frac{r^2}{a}\right)^2+y^2}\right.$$

$$\left.+\frac{2\,r^3}{a^3}\cdot\frac{\left(x-\frac{r^2}{a}\right)\left(x^2+y^2-\frac{r^2\,x}{a}\right)}{\left[\left(x-\frac{r^2}{a}\right)^2+y^2\right]^2}\right\}. \qquad (29)$$

This has the value $-\frac{\lambda}{a^2}$ at all points of the circumference, and gives us the flow function inside a circular disk in which there is a simple quadruplet with axis making an angle of 45° with the radius drawn through it.

It is to be noticed that (29) is the real part of the function

$$w=-\lambda\left\{\frac{1}{(z-a)^2}-\frac{r^4}{a^4}\cdot\frac{1}{\left(z-\frac{r^2}{a}\right)^2}-\frac{2\,r^2}{a^3}\cdot\frac{1}{z-\frac{r^2}{a}}\right\}, \qquad (30)$$

which appears in equation (28).

14. The flow function due to a simple quadruplet at the centre of a circular disk of radius r may be found by putting a equal to zero in (27). It is

$$\psi=-2\,\lambda\,x\,y\left\{\frac{1}{(x^2+y^2)^2}-\frac{1}{r^4}\right\},$$

and the corresponding w is $\frac{1}{z^2}+\frac{z^2}{r^4}$.

In general, consider the function

$$w=\frac{1}{z^n}+\frac{z^n}{r^{2n}}=\frac{r^{2n}+\rho^{2n}\,(\cos 2\,n\,\theta+i\,.\sin 2\,n\,\theta)}{r^{2n}\,.\,\rho^n\,(\cos n\,\theta+i\,.\sin n\,\theta)}$$

$$=\frac{r^{2n}\,.\cos n\,\theta+\rho^{2n}\,(\cos 2\,n\,\theta\,.\cos n\,\theta+\sin 2\,n\,\theta\,.\sin n\,\theta}{r^{2n}\,.\,\rho^n}$$

$$+\frac{i\,\{\rho^{2n}\,(\sin 2\,n\,\theta\,.\cos n\,\theta-\cos 2\,n\,\theta\,.\sin n\,\theta)-r^{2n}\sin n\,\theta\}}{r^{2n}\,\rho^n}$$

$$=\frac{r^{2n}+\rho^{2n}}{r^{2n}\,.\,\rho^n}\cos n\,\theta+\frac{i\,(\rho^{2n}-r^{2n})}{r^{2n}\,\rho^n}\sin n\,\theta. \qquad (31)$$

The function

$$\psi = \frac{(\rho^{2n} - r^{2n}) \sin n\,\theta}{r^{2n}\,\rho^{n}} \tag{32}$$

is constant along the circumference drawn about the origin with radius r, and is evidently the flow function due to a simple 2^{n+1}-plet at the centre of a circular disk.

15. The rational algebraic function $\frac{\chi(z)}{F(z)}$, where the numerator and denominator are algebraic polynomials involving only integral powers of z, can be put by simple division into the form of a rational algebraic polynomial in z plus the proper fraction, $\frac{f(z)}{F(z)}$, where the numerator is of degree at least one lower than the denominator. This proper fraction can be represented in the usual way as the sum of a series of fractions the numerators of which are in general complex constants and the denominators of the form $[z - (a + b\,i)]^{\kappa}$.

The real part of $\frac{f(z)}{F(z)}$ is therefore the velocity potential function of a collection of motors such that each has for its own velocity potential function the real part of a function of the form

$$\frac{\alpha + \beta\,i}{(z - (a + b\,i))^{\kappa}} \quad \text{or} \quad \frac{\mu\,(\cos\delta + i\,\sin\delta)}{(z - (a + b\,i))^{\kappa}}. \tag{33}$$

FIG. 11.

Let us take as the axis of a simple multiplet a line which, drawn as a diameter through the symbol which represents the motor, bisects the black portion nearest the axis of x. If this line goes through two black portions, the sense in which the direction of the axis is taken is of no consequence. If it goes through one black sector and one unshaded sector of the symbol, the direction shall be *from* the unshaded part *to* the black part. The simple motor, for instance, which has for its flow function the real factor of the imaginary part of $-\frac{1}{z^{\kappa}}$, has its axis coincident with the axis of x.

The values at the point (x, y) of the velocity components due to any motor at the point (a, b) must be equal respectively to the two velocity components at the point $(x - a, y - b)$ due to the same motor at the origin with axis parallel to its old direction.

If $\phi(x, y)$, $\psi(x, y)$ are the velocity potential and flow functions due to the motor at the origin, $\phi(x - a, y - b)$, $\psi(x - a, y - b)$, yield velocity components for the case of the same motor at (a, b) which satisfy the condition stated above.

If $$f(z) = \phi(x, y) + i\,\psi(x, y), \text{ however,}$$

$$f(z - a - b\,i) = \phi(x - a, y - b) + i \,.\, \psi(x - a, y - b),$$

and, as a particular case, $\dfrac{1}{[z - (a + b\,i)]^{\kappa}}$ and $\dfrac{1}{z^{\kappa}}$ correspond to two equal and similarly placed motors, one at the point (a, b), the other at the origin.

Let us now compare the motors the flow functions of which are the real factors of the imaginary parts of

$$\frac{1}{z^{\kappa}} \quad \text{and} \quad \frac{\alpha + \beta\,i}{z^{\kappa}}$$

respectively; that is, of

$$\frac{\operatorname{ces} \kappa\,\theta}{\rho^{\kappa}} \quad \text{and} \quad \frac{\mu \operatorname{cis} \delta \,.\, \operatorname{ces} \kappa\,\theta}{\rho^{\kappa}},$$

where $z = \rho(\cos\theta + i \,.\, \sin\theta)$, $\alpha + \beta\,i = \mu\,(\cos\delta + i \,.\, \sin\delta)$, and where $(\cos\delta + i \sin\delta)$ and $(\cos\theta - i \,.\, \sin\theta)$ are written $\operatorname{cis}\delta$ and $\operatorname{ces}\theta$ respectively.

The two flow functions are

$$\frac{-\sin\kappa\,\theta}{\rho^{\kappa}} \quad \text{and} \quad -\frac{\mu \,.\, \sin\kappa\left(\theta - \dfrac{\delta}{\kappa}\right)}{\rho^{\kappa}};$$

and the values at the point (r, θ) of the velocity components respectively parallel and perpendicular to the radius vector drawn from the origin are

$$-\frac{\kappa \,.\, \cos\kappa\,\theta}{\rho^{\kappa+1}} \quad \text{and} \quad \frac{\kappa \,.\, \sin\kappa\,\theta}{\rho^{\kappa+1}}$$

in the case of the first motor, and

$$-\frac{\mu\,\kappa\,.\,\cos\kappa\left(\theta-\frac{\delta}{\kappa}\right)}{\rho^{\kappa+1}} \quad \text{and} \quad \frac{\mu\,\kappa\,.\,\sin\kappa\left(\theta-\frac{\delta}{\kappa}\right)}{\rho^{\kappa+1}}$$

in the case of the second motor. The second motor gives at every point velocity components which the first motor gives at a point equally distant from the origin, but differing in vectorial angle from the first point by $\frac{\delta}{\kappa}$. The second motor is then equivalent to the first turned through the angle $\frac{\delta}{\kappa}$.

If, then, the simple motor which corresponds to the function $\frac{\mu}{z^\kappa}$ were transferred parallel to itself to the point (a, b) and then rotated counter-clockwise through the angle $\frac{\delta}{\kappa}$, it would correspond to the function $\frac{\alpha+\beta i}{[z-(a+b\,i)]^\kappa}$. It is to be noticed that a rotation of the motor corresponding to $\frac{\mu}{z^\kappa}$ through the angle $\frac{2\pi}{\kappa}$ would by reason of symmetry give the same motor, and multiplying $\frac{\mu}{z^\kappa}$ by i would turn the symbol representing the motor through half the angle which corresponds to a black sector.* The rational algebraic proper fraction $\frac{f(z)}{F(z)}$ corresponds then, in general, to a distribution of variously oriented simple multiplets, and the function $Az+\frac{f(z)}{F(z)}$, which frequently appears in two dimensional problems in magnetism, to a distribution of such multiplets in a uniform field.†

16. The real parts of the functions $-\frac{\lambda}{z^\kappa}$, $-\frac{\mu\text{ cis }\kappa\alpha}{z^\kappa}$, are the velocity potential functions which correspond to two simple multiplets of the κth order, L and M, of strengths respectively equal to λ and μ. Both L and M are situated at the origin. L's axis coincides with the axis of x, but M's axis makes with the axis of x the angle α.

If we superpose L upon M, we get

$$w=\frac{-(\lambda+\mu\,.\,\cos\kappa\alpha+i\,.\,\mu\,.\,\sin\kappa\alpha)}{z^\kappa}$$

$$=-\frac{\sigma\,.\,\text{cis }\tau}{z^\kappa}, \tag{34}$$

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* This explains the identity of equations (28) and (30).

† See, for instance, Maxwell's Treatise on Electricity and Magnetism, Vol. II. Figs. XV. and XVI.

where

$$\sigma^2 = \lambda^2 + \mu^2 + 2\,\lambda\,\mu \cos \kappa\, a, \tag{35}$$

$$\tau = \sin^{-1}\left\{ \frac{\mu \sin \kappa\, a}{\sqrt{\lambda^2 + \mu^2 + 2\,\lambda\,\mu \cos \kappa\, a}} \right\}. \tag{36}$$

This is a motor of the same kind as L and M. Its strength is σ, and its axis makes with the axis of x the angle $\frac{\tau}{\kappa}$. In the case of doublets, that is, when $\kappa = 1$, this result may be put into a simple form. If two doublets L and M exist together at a point O, and if the directions of the two straight lines OA, OB, show the directions of the axes of L and M respectively, and the lengths of OA and OB the strengths of L and M on some convenient scale, then the direction of the axis of the result of L and M will be given by the directions and the strengths of the resultant by the length of the diagonal of the parallelogram of which OA and OB are adjacent sides. Doublets then can be compounded and resolved by compounding and resolving their axes like forces or velocities.

17. Let there be any motor M at a distance a from the centre of a circumference of radius r drawn in a plane, and let the radius drawn through M be taken as axis of x. Let $\mu \,.\, \chi\,(x, y, a)$ be the flow function due to M, and its image in the circumference, existing together. If another motor B, of the same kind and strength as A but of opposite sign, exist at a point on the axis of x at a distance $a + \Delta a$ from the centre, the flow function due to B and its image together is

$$-\,\mu \,.\, \chi\,(x, y, a + \Delta\, a).$$

The flow function due to A, B, and their two images existing together is, therefore, $-\,\mu \,.\, \Delta_a\, \chi\,(x, y, a)$.

If now Δa be made to approach zero and μ to increase so that $\mu \,.\, \Delta a$ is equal to the constant λ, we get as the flow functions due to the resulting new motor at A and its image in the circumference

$$\psi = -\,\lambda \,.\, D_a\, \chi\,(x, y, a). \tag{37}$$

$F\,(z, a)$, of which ψ is the real factor of the imaginary part, is connected with $f\,(z, a)$, of which χ is the real factor of the imaginary part by the equation

$$F\,(z, a) = -\,\lambda \quad D_a\, f\,(z, a). \tag{38}$$

If, for instance, we apply (38) to

$$w = \mp \mu \left\{ \frac{1}{z - a} + \frac{r^2}{a^2} \cdot \frac{1}{z - \frac{r^2}{a}} \right\},$$

which yields (5), we get

$$\pm \lambda \left\{ \frac{1}{(z - a)^2} + \frac{r^2}{a^4} \cdot \frac{r^2 - 2a^2}{\left(z - \frac{r^2}{a}\right)^2} \right\},$$

which, after reduction, gives (30).

By means of (38) and other similar equations, a great number of cases of flow inside circular disks may be found.

Jefferson Physical Laboratory,
Cambridge, Mass., August 18, 1891.

XV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.

FOURTH PAPER.

By Theodore William Richards.

Presented June 10, 1891.

Table of Contents.

Introduction.

It will be remembered that recent investigation upon the atomic weight of copper has pointed toward the existence of a value for that constant very different from the one indicated by earlier determinations. During the winter of 1886–87 a number of experiments * were made in this Laboratory upon the replacement of silver from solutions of argentic nitrate by means of metallic copper; and during the following winter these were supported by similar series † involving material from different sources. The consistent verdict of all these experiments indicated a considerably higher atomic weight than that which had previously been accepted; but although the new method seemed to be in every way satisfactory, the presumption must nevertheless remain in favor of the older value until the presentation of more evi-

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* These Proceedings, XXII. 342.

† These Proceedings, XXIII. 177; Fres. Zeitschr., XXVIII. 392.

dence against it. Accordingly, another method of determination was devised, and the two distinct but concordant series of results obtained by this method fully confirmed the higher value. The aspect of the case was now wholly changed, — it presented two series of coincidences, of which one must necessarily be due to chance alone; and in such a case certainty can be reached only through a complete and intelligent reconciliation of the conflicting evidence. A careful examination of the possible sources of inaccuracy involved in all recent analyses failed to reveal the probability of a constant error greater than two or three units in the second decimal place. Therefore a complete examination of the older work seemed imperative, and the object of the present paper is to describe such a revision.

A brief review of earlier determinations is given in the first paper of the present series, but for the sake of convenient reference a complete summary is repeated below. On account of the present uncertainty with regard to the ratio of oxygen to hydrogen, the standard to which the figures in the following table are referred is the arbitrary one, $O = 16$; and this standard has been adopted throughout the present paper.

Atomic Weight of Copper.

$O = 16.000.$

Berzelius, 1828, from CuO (Pogg. Ann., VIII. 182.)	$Cu = 63.29$
Erdmann and Marchand, 1844, from CuO (J. pr. Chem., XXXI. 391.)	63.47
Dumas, 1859, from CuO and Cu_2S (?) (Ann. de Chim. et de Phys., [3], LV. 129, 198.)	63.50
Millon and Comaille, 1863, from CuO (Compt. Rend., LVII. 147; Fres. Zeitschr., II. 474.)	63.12
Hampe, 1874, from CuO	63.34
" " from $CuSO_4$ (Fres. Zeitschr., XIII. 352; XVI 458)	63.32
Baubigny, 1883, from $CuSO_4$ (Compt. Rend., XCVII. 854, 906.)	63.47
Shaw, 1886, through electrolytic equivalent	63.48
" " " " " corrected (Phil. Mag., [5], XXIII. 138.)	63.51
Richards, 1887, 1888, by relation to Silver (These Proceedings, XXII. 342; XXIII. 177.)	63.60
" 1890, from Cupric Bromide (two series) (These Proceedings, XXV. 195.)	63.61

The low value obtained by Hampe has been until recently universally accepted, because of the care employed in his analytical work, and the agreement between his results. Hence the present discussion will be confined almost entirely to the two substances which formed the bases of his operations.

The following values for the atomic weights of various elements entering into the present investigation will be assumed throughout the paper.

Oxygen	=	16.000	Hydrogen	=	1.008
Barium	=	137.10	Silver	=	107.930
Bromine	=	79.955	Sodium	=	23.053
Carbon	=	12.002	Sulphur	=	32.060

BALANCE AND WEIGHTS.

The balance used in the work to be described was made with especial care by Henry Troemner, of Philadelphia, and was procured particularly for the present research. The beam and pans are composed of aluminium, and all the remaining metal-work is plated with gold. By raising the centre of gravity, the pointer may be made to swing with great constancy as much as eight divisions of the scale for one tenth of a milligram; but since this degree of sensibility is far beyond the range of accuracy obtainable even in atomic weight investigation, the balance was usually adjusted so that the pointer moved ten divisions for a milligram. A reasonable increase in load altered this relation but slightly. The balance was kept in a small closet lined with curtains, and was protected as much as possible from changes in temperature. The air of the case was dried by means of potassic hydroxide and sulphuric acid, and large dishes of the former substance were kept in the closet outside.

The standard weights have already been described.* They were carefully rubbed with chamois skin and again compared before the present work. The slight corrections, which differed scarcely at all from those previously found, were applied to each weighing.

A double rider attachment upon the balance made the method of weighing by substitution accurate and easy; and accordingly this method was invariably adopted, except in the first series of experiments upon cupric sulphate. In general, the vessel to be weighed was carefully tared with an adjusted set of common gilded weights, and the

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* These Proceedings, XXV. 196.

vibrations of the pointer were noted. After the removal of the vessel standard weights were added to the left-hand pan until the same condition of equilibrium was reached. The vessel was then once more substituted for these weights, and any slight change of centre point was of course manifest at once. In the rare cases when such slight change appeared, the weights and vessel were alternately substituted for each other until constancy was reached. In the case of hygroscopic substances the already ascertained weights were first placed upon each scale pan, then the vessel was quickly removed from the desiccator and substituted for the standard weights, and, finally, the latter were again put in place.

All desiccators were allowed to remain in the closet with the balance three or four hours before the weighing, and objects were often weighed on successive days, to furnish assurance of constancy. In every case the barometer and thermometer were read, and any correction due to change of relative buoyancy amounting to more than the fiftieth of a milligram was applied to the result. With large vessels an invariable slight loss of weight, amounting sometimes to as much as one twentieth of a milligram, was noticed after the object had remained for some time upon the balance pan. The loss may have been due to the replacement of the perfectly dry air from the desiccator by the less completely dried air of the balance case. Possible error from this source was avoided by the employment of uniform conditions suited to the particular substance in hand.

All weighings were of course reduced to the vacuum standard by calculation from the specific gravities of the substances and weights involved.* Through the great kindness of Professor Mendenhall of Washington, two of the Laboratory's ten-gram weights (one of brass and one of platinum) have been compared as carefully as possible with the standards of the Washington Bureau of Weights and Measures. Five comparisons of the Sartorius ten-gram weight with these gave the following results for its value in vacuum: —

1891.		Grams.
February 4.	By comparison with the brass weight,	10.00025
March 4.	" " " platinum weight,	10.00025
March 14.	" " " " "	10.00026
June 12.	" " " " "	10.00026
June 12.	" " " " "	10.00024
	Average,	10.00025

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* These Proceedings, XXV. 196. Specific gravity of brass = 8.3.

The third and fifth of these comparisons were made with the balance in the condition of greatest sensibility, while the others were made exactly in the usual manner. It is not pretended, however, that all the weighings which follow have probable errors so small as these. The results are nevertheless an excellent gauge of efficiency of the balance, especially since the observations were made at widely varying temperatures and pressures. The correction involved, applying in the same proportion to all weighings, has been omitted from the following figures; but any weight given below may of course readily be reduced to the Washington standard by multiplication with the factor 1.000025.

I. The Analysis of Cupric Sulphate.

The only published analyses of cupric sulphate which have had for their object the determination of the atomic weight of copper are those previously mentioned. Hampe has very clearly described two extremely concordant electrolytic determinations of the copper contained in the so-called anhydrous salt. The greatest care had been taken to separate minute traces of metallic impurities from the preparation, which had been dried at 250° Centigrade; but apparently it was not realized that for the purpose in hand the retention of a trace of water by the salt was a much more serious possible cause of error than any other. Baubigny's analyses are less fully described, so that it is less easy to judge of their value. A different method, the conversion of cupric sulphate into the oxide by heat, was adopted for these experiments. The result was very different from that obtained by Hampe, but was more nearly accurate, because complicated with a less serious combination of constant errors.

The entire reconciliation of all these results, not only with each other, but also with the more recent analyses, involved the complete analysis and synthesis of cupric sulphate. A somewhat detailed account of the various operations is given below. Many of the less important points are necessarily omitted on account of the already too great accumulation of material, and many relations between the figures can be worked out by those whom they may interest. It is to be hoped that the effort to spare the overburdened literature of to-day any unnecessary additions may not have interfered with the clearness of the description. The first three series of experiments upon the analysis of cupric sulphate constituted a study of the effect of progressive refinement, and the first of the three perhaps hardly deserves a place in a paper upon atomic weights. Unless otherwise stated, the data are given in full.

Materials used in the Analysis.

Cupric Sulphate. — The substance used in the first series of experiments was partly prepared from very pure copper remaining from the cupric bromide research, and partly from other sources. It was perfectly neutral and reasonably pure. For the second and third series four hundred grams of the so-called "chemically pure" cupric sulphate of commerce were dissolved in a very large amount of water, and the solution was twice successively treated with a very small amount of potassic hydroxide in dilute solution; the mixture being occasionally shaken and allowed to stand each time for a week before decanting the clear supernatant liquid. One quarter of a gram of ammonic bromide was added to this liquid; and after standing two weeks the solution was carefully filtered, evaporated to very small bulk in a porcelain dish, and again filtered from the deposited basic salt. The finely divided crystals obtained from this solution by agitation and cooling with ice were drained with a reverse filter,* redissolved in hot water, and repeatedly recrystallized in platinum vessels. The first three mother liquors were rejected, but the later ones were all combined. After three more recrystallizations the substance contained in these mother liquors was dissolved in cold water and allowed to crystallize by slow evaporation in pure air. The preparation thus made was used in the second series of analyses.

The crystals obtained by eight successive crystallizations in platinum vessels were dissolved in cold water, and the salt was slowly recrystallized over sulphuric acid in a vacuum. The substance thus obtained was dissolved in water which had been distilled in a platinum retort, and after standing six days the perfectly clear solution was again brought to crystallization in a vacuum. These crystals were dried in a platinum dish over partially dehydrated cupric sulphate, and were used for the third series of experiments. The neutrality of each of these preparations was determined as nearly as possible by means of methyl orange, after the manner described in these Proceedings, Volume XXV., page 201.

Sodic Carbonate. — As sodic carbonate formed one of the chief bases for the determination of the sulphuric acid, its manufacture in a pure state was a matter of great importance. From the "chemically pure" material of commerce one may easily procure by five recrystallizations a material which gives no coloration with ammonic sulphy-

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* These Proceedings, XII. 124.

drate, nor, after neutralization, with potassic sulphocyanide.* Sodic sulphate and chloride are even more readily separated than traces of iron.

Three separate preparations of sodic carbonate were used in the course of the work. For the first series of comparatively crude experiments the solution of ordinary "chemically pure" material, which almost invariably contains a perceptible amount of finely divided solid matter, was after filtration twice recrystallized in a platinum dish. It was subsequently found advantageous to prevent the clogging of the filter by two or three preliminary recrystallizations, in the course of which most of the solid matter finds its way into the mother liquor.

The second sample of sodic carbonate was recrystallized six times after filtration. The vessels, rod, and reverse filter were all of platinum, and water was used which had been distilled in a platinum retort.

Besides all these precautions, several additional ones were taken in the preparation of the purest sample of sodic carbonate designed for the third series. The water used had been distilled four times: first alone, next over potassic permanganate, then over acid potassic sulphate, and finally in a platinum still without the addition of foreign matter. Every precaution was taken to exclude dust and acid fumes, and the sodic carbonate was recrystallized ten times after filtration. The salt prepared in this way gives an absolutely odorless warm concentrated solution. The second and third samples gave essentially identical results. Each of the three preparations was pure snow-white, whether fused or unfused; each gave a perfectly clear and colorless solution with water; and not even the first gave the least test for hydrochloric or sulphuric acid.

On the other hand, as Stas has already indicated, the most elaborate precautions are unable to free sodic carbonate wholly from traces of silica and a basic oxide, which is probably alumina. The former impurity was determined in the usual manner. The alumina and silica were determined together in new portions of the salt by exact neutralization with hydrochloric or sulphuric acids, ignition of the evaporated product, and weighing of the insoluble residue. Phenol phthaleïn was used to determine the neutral point, and hence the

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* Stas appears once or twice to have had more difficulty in accomplishing this result. At other times his experience seems to have coincided with that described above. Compare Aronstein's translation (1867), pp. 112, 270, with p. 275.

insoluble bases present were necessarily precipitated. It is needless to state that the operations were conducted in platinum vessels. Neglecting two determinations which were vitiated by known impurity, the weight of total residue obtained varied from 0.15 to 0.41 milligram, while the weight of sodic carbonate taken varied from 1.02 to 3.06 grams. The average of twenty determinations showed about thirteen parts of impurity to exist in one hundred thousand parts of the salt. Silica constituted about forty per cent of this impurity. The third specimen did not differ essentially from the second on these averages. Owing to the slight solubility of silica in sodic chloride solutions,* the observed amount of this impurity may be slightly too low, but for the present purpose the correction is unimportant. The filter papers used in this part of the investigation left upon ignition an ash of 0.00004 gram.

Since the silica and alumina are probably present as sodic silicate and aluminate in the original carbonate, and may be considered as replacing carbon dioxide molecule for molecule, it is evident that the correction to be applied will not equal the whole weight of the residue. Upon this assumption the correction when phenol phthaleïn is used as an indicator amounts to about half the weight of the impurity, or about 0.007% of the weight of the sodic carbonate. Toward methyl orange aluminic hydroxide is alkaline; hence in this case the errors due to the two impurities tend to counterbalance each other, and the correction may be omitted. The presence of a small amount of alumina thus explains the slight difference observed later between the results obtained with these two indicators.

The crystallized sodic carbonate was dried over pure boiled sulphuric acid in a vacuum, and subsequently ignited to a dull red heat in a double crucible over a Berzelius spirit lamp. The latter apparatus was employed in order to avoid the possible introduction of impurity from illuminating gas. It was found that the salt could be ignited to perfectly constant weight at any temperature between dull redness and its fusing point. The light powder contracts and "sinters together" at a low red heat, and then remains essentially unchanged in weight until it melts. The unfused salt was not observed to gain perceptibly in weight upon an hour's exposure to the air of the balance case; upon the other hand, the fused salt, which of course was never used as a basis of determination, was markedly hygroscopic.

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* Stas, Aronstein's translation, p. 279. In this place the correction is applied to sodic chloride, but not to the nitrate formed from it.

Acids. — The chemically pure hydrochloric and nitric acids were each distilled three times successively in a platinum still. Large quantities evaporated in open dishes left unweighable and scarcely visible residues. The insignificant amount of the residues was a proof of the purity of the air, as well as of the acids. Neither acid gave a test for iron, and the nitric acid contained no chlorine even at the beginning of the operations.

Since the platinum still was very large, it was found more convenient to distil sulphuric acid from a small hard glass retort heated by a ring burner, immediately before it was needed. After three such distillations, a preparation was obtained which left no weighable residue upon the evaporation of any quantity used in the work.

All sulphuric acid used for drying was boiled with ammonic sulphate.

In order to keep the air of the laboratory quite pure, during the greater part of the time neither volatile acids nor ammonia were allowed in the room devoted to the investigation, and all available precautions were taken against dust.

Indicators. — As is well known, the salts of most of the heavier metals are acid toward phenol phthaleïn and neutral toward methyl orange. The most important consequence of this relation has already been pointed out. When the former indicator was used, the slightly acidified solution was of course first freed from carbonic anhydride by long continued heating upon the steam bath, and the end point was determined with pure caustic alkali. It is a noteworthy fact, that methyl orange is useless in very concentrated solutions of sodic sulphate, the color change becoming apparent only upon dilution. This indicator is naturally less serviceable in the presence of a strong color like that of a copper salt. It is less sensitive with cupric sulphate than with cupric bromide. In such cases as these, colorimetric comparison can alone afford accurate results; but even here the effect of a personal equation must be more or less perceptible.

Since the amount of either indicator used in any one case was not more than the thirtieth of a milligram, it could not have seriously influenced subsequent operations with the solution.

Water. — The distilled water taken hot from the tin-lined condenser around a steam-drying oven contained no ammonia discoverable by Nessler's reagent, and in the first crude experiments this water was used without further treatment. After having been once more distilled in a platinum still, it appeared to be very pure. The first portions of the distillate were rejected, although no ammonia was found in them. The water left absolutely no trace of residue upon evaporation, even after long standing. Such doubly distilled water was used in the second series of experiments.

For the third series all the water used, even for minor operations, was distilled four times: first alone, then over alkaline potassic permanganate, next over acid potassic sulphate, and finally once more alone in the platinum still. Since this water was not different in any of its properties from the second preparation, the last refinements were probably unnecessary; and in later work water which had been distilled only twice was used.

The value of the present work has been largely increased by the unlimited supply of platinum ware placed at the disposal of the writer through the kindness of Professor Cooke. Because of the large size of some of the retorts and bottles, it was impossible to free these vessels from iron after the method of Stas. Accordingly they were digested alternately with strong hydrochloric and nitric acids until pure acid which had remained in them for days gave no test for iron after evaporation upon the steam bath.

Smaller vessels were freed from iron in the usual manner, by treatment with the vapors of ammonic chloride at a red heat, as well as with fused acid potassic sulphate. They were usually protected during ignition by an outer crucible, from which they were separated by a coil of platinum wire. Crucibles weighing twenty grams rarely showed a variation of more than one twentieth of a milligram between the weights taken before and after any ordinary operations, excepting when ignited with cupric oxide under conditions which will be explained later.

Description of Analyses.

FIRST SERIES.

It is evident that the most probable constant error in Hampe's work lay in the great hygroscopic power of cupric sulphate dried at 250°. A possible means of detecting such error existed in the use of the crystallized salt as a starting point. This salt was therefore coarsely powdered, dried to constant weight over a mixture of crystallized and partially dehydrated cupric sulphate, and analyzed by electrolysis in the usual fashion. Although the crystalline powder must have contained occluded water, the quantity of copper found in several samples from different sources was much larger than that demanded by the old atomic weight, and closely approached the theoretical quantity based upon the new value.

In the third experiment the weight of water lost by heating the salt to constant weight in the manner described by Hampe [*] was also determined, and this amount proved to be nearly three tenths of a per cent less than it should have been according to any hypothesis. Since larger crystals of cupric sulphate exposed to air above the desiccating mixture already mentioned lost none of their lustre, and since the salt under these conditions comes to perfectly constant weight, it seemed highly probable that the apparent deficiency of crystal water was due to occlusion in the so-called anhydrous salt, and not to any previous efflorescence of the crystals.

The sulphuric acid produced during the electrolysis [†] was preserved in each case, and approximately determined by means of the first preparation of sodic carbonate; also afterwards by the evaporation of the solution of sodic sulphate. Since the manipulation was more or less imperfect, and the materials and water not quite pure, it is thought unnecessary to include these somewhat bulky data in full here, but the evidence which they furnished was conclusive upon one point. The percentage of acid was not equal to the complement of the other percentages. In other words, over one tenth of a per cent of material had not been determined.

	Found.	Theory Cu = 63.60.	Theory Cu = 63.33.
Percentage of Water . . .	35.958	36.0695	36.109
" " Copper . .	25.455	25.4665	25.385
" " SO_4 . . .	38.46±	38.464	38.506
Total	99.87	100.000	100.000

It is seen that we are dealing, not with infinitesimals, but with grave error evident to the crudest analysis. The reason for the deficiency has already been suggested, but the proof is yet wanting.

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[*] *Loc. cit.*

[†] In this connection it may be noted that Hart and Croasdale have quite independently used the sulphuric acid thus formed as a basis of alkalimetric analysis. (Chem. News, LXIII 93, 1891.) The idea appears to be a good one

The ratio between the copper and the sulphuric acid, or rather between the copper and sodic carbonate on the one hand and sodic sulphate on the other, affords a new twofold basis for the calculation of the atomic weight of copper. This basis is entirely independent of the always uncertain weight of the cupric sulphate and the objectionable method of calculation from difference. The results correspond to the new atomic weight, but the complete discussion of this phase of the subject will be reserved until more definite data have been given. It is interesting to note that these comparatively crude experiments differ only by one or two units in the second decimal place of the result from the far more carefully executed work yet to be described.

ANALYSIS OF CUPRIC SULPHATE. — FIRST SERIES: DATA AND RESULTS.

Weights reduced to Vacuum Standard.

No. of Experiment.	Weight Cupric Sulphate (cryst.).	Weight $CuSO_4$ (250°) found.	Weight Copper found.	Per Cent Water lost at 250°.	Per Cent Copper.
1	2.8815	....	0.7337	....	25.462
2	2.7152	....	0.6911	....	25.452
3	3.4639	2.2184	0.8817	35.958	25.454
			Average . . .	35.958	25.455

SECOND SERIES.

Although from the earlier experiments it appeared that the deficiency in the sum of the analytical results might be explained by the hypothesis of the existence of water in the so-called anhydrous cupric sulphate, it was possible that at least a part of this deficiency might be due to experimental error. The next step of the research was therefore to start again upon a more refined basis. It was important, too, that some proof of the above mentioned hypothesis more definite than an indirect inference should be obtained. The clearest idea of the various operations may probably be acquired through a detailed statement of one of the experiments, and accordingly such a statement is given below.

Experiment 4. — The cupric sulphate,* having been cautiously powdered in an agate mortar and dried to constant weight over the desiccating mixture already described, was gradually heated to 255° in a platinum crucible with a very closely fitting lid.

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* See page 245 of this paper.

Grams.
Weight of crucible + $CuSO_4 . 5 H_2O$ = 23.36188
" " alone = 20.30300
" cupric sulphate in air = 3.05888
Correction to vacuum (Sp. gr. = 2.274) = .00118
Corrected weight $CuSO_4 . 5 H_2O$, in vacuum = 3.06006

Weight crucible + $CuSO_4$ dried for three hours at 255° = 22.26243
" " dried for two hours more = 22.26233

The crucible and contents gained in weight upon the balance pan at a rate of only one tenth of a milligram in four minutes, and hence the last weighing is without doubt sufficiently accurate. When the weight had thus become constant, twenty drops of strong pure sulphuric acid were added to the white powder, and the whole was kept at a temperature of 365° for three and one half hours in a suitable air bath composed of a nest of porcelain crucibles. An air thermometer was used in measuring the temperature.

Grams.
Weight of crucible and contents = 22.25905
The same, after reheating for four hours with six drops more of H_2SO_4 = 22.25900
Weight in air of cupric sulphate dried at 365° = 1.95600
Weight in vacuum of cupric sulphate (Sp. gr.[*] = 3.61) = 1.95637
Loss of weight between 255° and 365° = .00333

The crucible and contents gained in weight even less rapidly than before.

This experiment shows that the so-called anhydrous cupric sulphate of Hampe *loses about seventeen one-hundredths of a per cent of its weight* when subjected to the temperature of the boiling point of mercury; a loss nearly equal to the deficiency which we are seeking to explain. The residual salt may be slowly dissolved in water without the need of very great caution. It gives a perfectly clear solution, which is neutral to methyl orange and does not deposit basic salt even upon indefinite standing. These facts alone show that the decrease in weight was not due to loss of acid, but a much more definite proof of this point is given later.

For electrolysis, the clear solution of the 1.95637 grams of cupric sulphate was transferred to a large platinum crucible. This crucible had been previously coated inside with pure copper, washed with

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[*] This is a mean of the results of Hampe and Karsten.

water and alcohol, and dried at 103°. The crucible was supported upon a platinum triangle in the interior of a large breaker, and was covered by a watch glass into which was fused the positive electrode. The wires conducting the current into the beaker were of platinum. The whole apparatus was covered with a large watch-glass, which effectually excluded impurity. Several times before the conclusion of the electrolysis the drops adhering to the inner watch-glass were washed back into the crucible by means of apparatus especially adapted for the purpose. After the maintenance for 120 hours of a weak current,[*] the electrolysis was interrupted, and every trace of the acid in the crucible was washed as rapidly as was consistent with scrupulous care into a large platinum bottle. The crucible was then washed with pure alcohol, dried at 103°, and finally weighed.

Grams.
Crucible + Cu before electrolysis (Bar. = 767 ; $t^\circ = 20^\circ$) = 36.12120
" + additional Cu after (Bar. = 750 ; $t^\circ = 20^\circ$) = 36.90000
Apparent weight of copper = 0.77880
Correction for change in temperature and pressure = + .00007
" to vacuum = – .00001
True weight of copper in vacuum = .77886

Per Cent.
Percentage of copper in $CuSO_4 . 5 H_2O$ = 25.452
" " " $CuSO_4$ dried at 255° = 39.744
" " " " dried at 250° (Hampe) = 39.725
" " " " dried at 365° = 39.811

Further comment here is unnecessary.

The earlier experiments had already shown approximately the equivalent ratio of sodic carbonate to copper. Accordingly a very little less than the amount of sodic carbonate corresponding to the data above was carefully weighed out from the second sample of this material, and the salt was ignited at a dull red heat until constant in weight.[†]

Grams.
Weight crucible + Na_2CO_3 = 21.60095
" " alone = 20.30260
" sodic carbonate in air = 1.29835
" " " in vacuum (Sp. gr. = 2.466) = 1.29880

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[*] These Proceedings, XXV. 202.

[†] See description of sodic carbonate, page 247 of this paper.

The sodic carbonate was dissolved in water and poured into the very dilute solution of sulphuric acid which had been formed by the electrolysis. The lid of the crucible, as well as that vessel itself, was very thoroughly washed with water. On account of the great dilution of the liquid, carbonic anhydride was not at once set free, but upon warming for six or eight hours upon the steam bath it was easily expelled. During this operation the platinum flask was of course suitably covered, a Gooch crucible being found most convenient for this purpose.

When gas evolution had long ceased, the solution was wholly transferred to a large platinum dish, and was evaporated on the steam bath to a volume of about fifty cubic centimeters. The very slight excess of acid was then titrated by means of sodic hydroxide, using methyl orange as an indicator, and was found to require 0.09 cubic centimeter of a decinormal solution for neutralization. The probable error of the end point was not greater than one drop, or one ten-thousandth part of the sodic carbonate present.

		Grams.
Sodic carbonate weighed out	=	1.2988
" " added in titration	=	0.0005
" " required (in vacuum)	=	1.2993
Cupric sulphate taken ($CuSO_4 \,.\, 5\, H_2O$)	=	3.06006
Copper found in " "	=	.77886

Per cent of SO_4 in $CuSO_4 \,.\, 5\, H_2O = 38.439$

Atomic weight of copper:

$$Na_2CO_3 : Cu = 106.108 : 63.606$$

In transferring the sodic sulphate from the evaporating dish to the capacious platinum crucible in which it was to be weighed, the precaution of washing with water which had been thoroughly boiled was absolutely essential to prevent the possibility of subsequent mechanical loss during evaporation. At best, the concentration of a solution in an open crucible over the steam bath is an unsatisfactory operation, and accordingly for the third series a new method was devised. The water left the sodic sulphate very slowly; but in the end it evaporated so completely that after covering there was a scarcely audible decrepitation on heating the crucible to redness. The pure white sodic sulphate was finally fused at a bright red heat. During this last operation the salt occasionally became tinged with a slightly yellowish hue, due probably to a trace of iron from the platinum vessels; but the purest specimens remained wholly colorless. The salt lost only one or two tenths of a milligram during the fusion. A drop of very dilute permanganate solution was not decolorized by the solution of the residual salt, showing that no reduction had taken place. A very small amount of insoluble residue, consisting of the apparently unavoidable impurity in the sodic carbonate together with any iron or copper which might be present, was determined in each case; and the amount was subtracted from the weight of sodic sulphate. Naturally, besides this, it is necessary to subtract the amount of salt corresponding to the *acid* added in titrating back and forth when determining the end point of the acidimetric reaction. This end point had been taken as the average of a number of readings. Below are the data of the experiment under discussion.

		Grams.
Weight of crucible + Na_2SO_4 (etc.)	=	18.67040
" " alone	=	16.92594
Uncorrected weight of Na_2SO_4	=	1.74446
Subtract weight of salt added in titration	=	.00362
" " insoluble residue	=	.00034
Corrected weight of Na_2SO_4 in air	=	1.74050
Correction to vacuum (Sp. gr. = 2.631)	=	+.00063
Weight Na_2SO_4 in vacuum	=	1.74113

Per cent of SO_4 in $CuSO_4 . 5 H_2O$ = 38.445
" " " " found above = 38.439

Atomic weight of copper (if Na_2SO_4 = 142.166, from table):

Weight Na_2SO_4 : weight Cu = 142.166 : 63.595.

No copper was found in the solution of the sodic sulphate, and a minute trace only in the insoluble residue.

The object of the second experiment of the series was to determine whether the method of weighing cupric sulphate in a tightly covered crucible was an accurate one. The determination was in every respect modelled after the mode of procedure adopted by Hampe, a tightly stoppered weighing-bottle being used to contain the salt. The result sufficiently confirmed the previous experiment. For later experiments a crucible was accordingly used, since the evaporation of sulphuric acid at high temperatures is much more feasible in such an apparatus. A mishap prevented the accurate determination of the acid.

For the third experiment, a much larger amount of material was used, the method being essentially that of the first experiment. The large crucible of one hundred and fifty cubic centimeters' capacity used for the electrolysis was not previously coated with copper. The end point of the acidimetric determination was taken with both phenol phthaleïn and methyl orange, the color change with the latter indicator being rather unsatisfactory in the presence of so large an amount of dissolved substance. The amount of insoluble residue found in the sodic sulphate was only 0.0003 gram; it contained no trace of copper. The results showed that little was to be gained by the use of larger quantities of substance, since the unavoidable errors of quantitative work were multiplied nearly in proportion to the quantities of material. Mechanical errors are at the present day inessential compared with the constant ones which complicate so many analyses. It is obvious that a far more accurate result could be obtained from four tenths of a gram of really anhydrous cupric sulphate, than from four hundred grams of a substance still retaining nearly two tenths of a per cent of water.

Adding in the small amount of water which is lost by cupric sulphate between 255° and 365°, the percentage composition of the crystallized salt, as indicated by the second series of analyses, gives a much more satisfactory total result than before: —

Water lost at 255°	= 35.960
Additional water lost at 365°	= 0.108
Copper	= 25.450
Sulphuric acid radical	= 38.436
Total	= 99.954

Although greatly improved, the analysis still leaves much to be desired. Even in materials prepared with the described precautions, traces of impurity were manifest. In the last experiment, where a large amount of material was used, a few minute spots, which might have been arsenic, appeared on the clear surface of the electrolytic copper, and traces of a brownish coloration were observed upon the positive pole. Both of these impurities were so infinitesimal in amount that they could not reasonably have been expected seriously to affect the final result; but the thought that they might be responsible for a part of the remaining deficiency prompted the execution of a still more elaborate series of experiments. The data and results of the second series are appended: —

ANALYSIS OF CUPRIC SULPHATE. — SECOND SERIES: DATA.

Weights reduced to Vacuum Standard.

No. of Experiment.	$CuSO_4 5H_2O$ taken.	$CuSO_4$ (260°) taken.	$CuSO_4$ (360°) found.	Metallic Copper found.	Sodic Carbonate required.		Sodic Sulphate found.
					Methyl Orange.	Phenol Phthalein.	
	grams.	grams.	grams.	grams.	grams.	grams.	grams.
4	3.06006	1.9597	1.95637	0.77886	1.2993	....	1.7411
5	2.81840	1.8048	....	0.71740			
6	7.50490	4.8064	4.79826	1.90973	3.1859	3.1865	4.2679

SECOND SERIES: RESULTS.

No. of Experiment.	Water lost at 260°.	Additional loss at 360°.	Total Per Cent of Water (360°).	Per Cent of Copper.	Per Cent of SO_4 by Na_2CO_3 (average).	Per Cent of SO_4 by Na_2SO_4.
4	35.959	0.109	36.068	25.452	38.439	38.444
5	35.964	....	....	25.454		
6	35.957	0.108	36.065	25.446	38.435	38.424
Averages	35.960	0.108	36.067	25.450	38.437	38.434

THIRD SERIES.

It is only by gradual approach that very accurate quantitative work may be realized, and the earlier series were absolutely necessary as a training and preparation for the present one. This series had for its object, not only an investigation of the effect of increased refinement, but also a definite proof that the amount of acid present in cupric sulphate was unaffected by the operations involved in the dehydration of the salt. To this end the first sample was not dehydrated at all, the second was heated only to 250°, and the third was exposed to the full heat of 365°, after the addition of sulphuric acid. Since the percentage of acid found in these samples did not vary beyond a reasonable limit of error, the proof is satisfactory.

The additional precautions taken in the preparation of the materials have already been mentioned under appropriate heads. Besides these, many refinements of manipulation were employed, too numerous to be fully described. For example, phosphorous pentoxide was used as a drying agent in the desiccator, and immediately after the introduction of a hot crucible the air was exhausted with a good air-pump and readmitted through a series of drying tubes. This method of course absolutely prevents the absorption of moisture by the contents of the crucible, while cooling.

Again, in the ninth experiment, the solution of the perfectly neutral sodic sulphate was transferred to a small flask, heated to 103°, and evaporated by means of a current of pure dry air. When dry, the sulphate was gently ignited and weighed in the flask, and subsequently fused in a platinum crucible. The flask lost 0.00010 gram during the operations, and the sodic sulphate lost 0.0003 gram upon fusion. With the exception of the small flask, all the apparatus was of platinum. The sodic sulphate formed in the second experiment, and the sodic carbonate required in the third, were not determined.

The last experiment of the series was not of the same grade of refinement with the others. It is only included here because the same preparation of cupric sulphate was used in its execution.

The determination of the sulphuric acid by still another method was the object of this experiment. Baric sulphate was precipitated from a boiling solution of cupric sulphate strongly acidified with hydrochloric acid. After weighing as usual, the perfectly white precipitate was fused with pure sodic carbonate, and the resulting cake thoroughly lixiviated with boiling water and dilute sodic carbonate solution. In the filtrate, the chlorine, which had been originally present as baric chloride occluded in the sulphate, was determined in the usual manner. Traces of baric sulphate and argentic chloride must have been dissolved in the wash water, but these errors tend to counterbalance one another, and hence no correction was made for them. Finally, the weight of baric chloride, calculated from the amount of chlorine found, was subtracted from the weight of baric sulphate; and from the corrected weight thus obtained the percentage of sulphuric acid in cupric sulphate was calculated. The astounding agreement of this experiment with the others may be nothing more than accident. In any case, the uncertainty of the atomic weight of barium, and the very unsatisfactory nature of baric sulphate, combine to make a repetition of the experiment of little value for the present purpose; but the method seems to be of value, and will form a subject of future investigation in this Laboratory. It is well known that baric sulphate has great power of occluding many salts, but few experimenters seem to have realized that the occlusion of most metallic sulphates tends to *decrease* the amount of precipitate obtained. This fact was recognized by Professor Jannasch and the writer[*] in 1889, and would influence the controversy between Ostwald[†] and Kruss.[‡] The occlusion of baric chloride of course increases the amount of precipitate when sulphuric acid is to be determined, and diminishes it when barium is to be determined. With care this last error may be reduced to a very small amount, but it is doubtful if it has ever been wholly avoided. A trace only of copper was found in the precipitate obtained in the experiment described above, showing that cupric chloride is not occluded to any essential extent.

In spite of the fact that the important analyses of the third series were far more carefully performed than those of the second, the result was no more satisfactory than before. It was therefore apparent that a point had been reached beyond which further refinement was unavailing, and that the reason of the discrepancy must be sought, not in accidental or variable impurity, but rather in some property inherent in the purest cupric sulphate.

ANALYSIS OF CUPRIC SULPHATE. — THIRD SERIES: DATA.

Weights reduced to Vacuum Standard.

No. of Experiment.	$CuSO_4 . 5 H_2O$ taken.	$CuSO_4$ found.	Metallic Cu found.	Na_2CO_3 found by Methyl Orange.	Na_2CO_3 found by Phenol Phthalein.	Sodic Sulphate found.
	grams.	grams.	grams.	grams.	grams.	grams.
7	2.88307	....	0.73380	1.2242	1.22435	1.63994
8	3.62913	at 260° 2.32373	0.92344	1.5407	1.54080	
9	5.81352	at 370° ± 3.71680	1.47926	....	....	3.30658
	$CuSO_4 . 5 H_2O$ taken.		Baric Sulphate found (uncor.).	Argentic Chloride found.	Baric Chloride calculated.	Baric Sulphate corrected.
	grams.		grams.	grams.	grams.	grams.
10	3.1902		2.9967	0.0284	0.0206	2.9761

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[*] J. für prakt. Chemie, XXXIX. 321 (1889).

[†] Lehrbuch der Allgem. Chem., I. 53.

[‡] Annalen, CCLXII. 49.

THIRD SERIES: RESULTS.

No. of Experiment.	Water lost at 260°.	Water lost at 370°±.	Copper found.	SO_4 found from Na_2CO_3 (average).	SO_4 found from Na_2SO_4.
7	....	....	25.452	38.443	38.433
8	35.970	....	25.446	38.435	
9	....	36.067	25.445	....	38.431
10					From Baric Sulphate. 38.434
Average	35.970	36.067	25.448	38.439	38.433

PERCENTAGE COMPOSITION OF CUPRIC SULPHATE.

	Second Series.	Third Series.	Theoretical.	
			Cu = 63.60.	Cu = 63.33.
Water	36.068	36.067	36.0695	36.109
Copper	25.450	25.448	25.4665	25.385
SO_4	38.436	38.436	38.464	38.506
	99.954	99.951	100.000	100.000

The Cause of the Deficiency.

It was by no means easy to trace the cause of the disappearance of less than one two-thousandth part of the material to its true source.

The notable agreement between the percentages of water given in the first three columns of figures immediately above of course suggested the possibility of a loss of copper and sulphuric acid during the electrolysis; and it became an important matter to test the point.

Accordingly weighed portions of a dilute solution of pure sulphuric acid were estimated with weighed amounts of sodic carbonate. Other portions of the same solution, weighed alternately with the previous ones, were then evaporated over the water bath with small amounts of cupric nitrate and successive additions of water. The cupric sulphate formed by this treatment was wholly decomposed by electrolysis, and the resulting sulphuric acid was determined exactly in the usual manner. The comparison of the acid solution before and after electrolysis is capable of showing at once whether any sulphuric acid was mechanically or chemically lost during the process. If any nitric acid had been held by the sulphuric acid in the second case, it could not have escaped decomposition during the electrolysis.

Following are the results: —

STRENGTH OF H_2SO_4 BEFORE ELECTROLYSIS.

Weights reduced to Vacuum.

Number of Experiment.	Solution taken.	Na_2CO_3 required.	Na_2CO_3 for 10.000 grams Solution.
	grams.	grams.	grams.
11	5.5932	1.0175	1.81917
12	11.4175	2.0768	1.81896
		Average . . .	1.81906

STRENGTH OF H_2SO_4 AFTER ELECTROLYSIS.

Weights reduced to Vacuum.

Number of Experiment.	Solution taken.	Na_2CO_3 required.	Na_2CO_3 for 10.000 grams Solution.
	grams.	grams.	grams.
13	16.8214	3.0592	1.81865
14	5.5612	1.0115	1.81886
		Average . . .	1.81876

Difference between averages . . . 0.0003.

Known mishaps tended to make the first experiments of each of the two groups respectively too high and too low. It is seen that the second experiments gave nearly identical results. Considering the increased transference and manipulation involved in the second group, the conclusion seems to be warranted that little if any sulphuric acid is lost during electrolysis.

In order to prove like relations with regard to copper a similar method was adopted. Weighed amounts of electrolytic copper were dissolved in pure nitric acid in a flask provided with bulb tubes for the condensation of spray. The cupric nitrate was then evaporated with an excess of sulphuric acid upon the water bath, and the cupric sulphate was electrolyzed as usual.

ELECTROLYSIS OF COPPER.

Number of Experiment.	Copper taken.	Copper found.	Loss of Metal.
	grams.	grams.	grams.
15	1.24156	1.24139	0.00017
16	1.00613	1.00600	0.00013

Here again, the manipulation was so much more elaborate than in a simple electrolysis that it is difficult to decide where the slight loss took place. In another experiment (No. 17) both copper and sulphuric acid were weighed before and afterward, but the experimental operations were so doubly involved that the determination was of very doubtful value. The result was not materially different from the others, however. The significant portions of the data are given in another place.*

In the course of these experiments it was found that a compact and brilliant copper film may be safely washed by decantation if sulphuric acid alone is present. Indeed, during most of the preceding determinations this method was adopted to insure complete collection of the acid, and in only one case (Experiment 7) was as much as one twentieth of a milligram of copper found in the filtrate. In this case that amount was added to the larger quantity, and the sum is given in the table. Potassic ferrocyanide was the reagent used in the colorimetric tests.

Assuming the deficiency of copper and acid as found above to represent a real loss during electrolysis, the composition of cupric sulphate would be: —

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* Page 268.

	Uncorrected.	Corrected.
Water	36.067	36.067
Copper	25.449	25.452
SO_4	38.435	38.442
	99.951	99.961

That is to say, an undoubtedly excessive value for this correction would account for only one fifth of the deficiency for which explanation was sought. The correction is at best very doubtful, and it is not applied in the final calculation of the atomic weight. Its application would make no essential difference in the final result, but would render the individual variations much less marked.

The only probable interpretation of the deficiency now lay in the assumption that cupric sulphate still held a volatile impurity at 360°. Such an amount of any non-volatile foreign substance would have increased the weight of sodic sulphate found at the conclusion of the analysis by about eight one-hundredths of one per cent, an amount entirely too large to escape detection. Besides, such a source of error had already been shown to be unlikely.

After it had been experimentally proved that cupric sulphate had no tendency to hold ammonic sulphate at 370°, the hypothesis of the occlusion of a small amount of water became the last resource. At first sight it seems improbable that any material could hold appreciable quantities of water in the presence of sulphuric acid when so strongly heated. But it must be remembered that at this temperature the acid is dissociated, and water is actually present in the vapor. It was hoped that sulphur trioxide might be more efficient as a dehydrating agent, but a single experiment (No. 18) showed that cupric sulphate possessed more affinity for water even at 300° than did the sulphur trioxide. 2.3787 grams (in vacuum) of cupric sulphate lost 0.8554 gram in weight on heating to about 300° in a glass tube under a current of dry air. Upon continuing the application of heat in air charged with sulphuric anhydride from Nordhausen acid, no essential change in weight was observed. The apparatus was somewhat complicated in order to avoid rubber connections, but a description of it is superfluous. The total loss was 35.962 per cent of the weight taken.

Experiments showed that between 360° and 400° cupric sulphate does not essentially lose in weight. For example (No. 19 or 23), 1.28563 grams of the substance dried at the former temperature weighed 1.28558 grams after heating for ten hours at 400°. At the temperature of dull redness the salt slowly decomposes.

If the loss of weight during this decomposition could be compared with the deficiency of sulphuric acid in the residue, it is evident that an indirect means would be at hand for the detection of a possible simultaneous loss of water. Such a circuitous road seemed to be the only one open to the present search.

In the series of experiments tabulated below, pure cupric sulphate was heated in the usual manner to 250°, and then after the addition of sulphuric acid to 400°, until the salt became constant in weight. The heat was then increased to dull redness, and after cooling the loss of weight was determined. Upon solution of the residue in water a small amount of basic salt was naturally deposited. Since the filtrate was apparently quite normal, it is evident that the amount of sulphuric acid necessary exactly to dissolve this precipitate must have been equivalent to the anhydride driven off.

After standing a considerable time, the basic salt was carefully filtered off and a measured amount of twentieth normal acid was used for its solution. The crucible used for the ignition was also washed with a measured quantity of acid. The clear solutions were all combined, and the excess of acid was determined by sodic hydroxide and methyl orange. Since the loss of weight upon ignition was noticeably more than the amount of anhydride corresponding to the quantity of sulphuric acid used to dissolve the basic salt, something beside sulphur trioxide must have been expelled by the heat.

The last column of the table gives the difference between the loss of weight of the cupric sulphate and the amount of sulphuric anhydride required to dissolve the basic salt, expressed in percentage of the original crystallized compound. This difference probably represents a small amount of water held even at 400°. The results showed a very noticeable variation, and at first sight appeared somewhat unsatisfactory. The first two experiments agreed well with each other, and were apparently very trustworthy. In the third, on the other hand, the amount of basic salt was so large as greatly to interfere with the accuracy of the result. In Experiment 23 the loss of weight upon ignition was so very large, amounting to about three per cent of the anhydrous sulphate, that the experiment was rejected. After such a failure, it was natural that the next sample should not have been heated enough. This result is hence probably too low. The last experiment was more carefully regulated, and is more trustworthy. In this case the cupric sulphate was heated for an hour at very dull redness.

Action of Heat upon Cupric Sulphate.

Weights reduced to Vacuum.

Number of Experiment.	Weight of $CuSO_4 . 5 H_2O$.	Weight of $CuSO_4$ [260°].	Weight of $CuSO_4$ [400°].	Weight after Ignition at dull Redness.	Loss between 400° and Redness.	$\frac{1}{20}$ normal H_2SO_4 required for Basic Salt.		Per Cent of $CuSO_4 . 5 H_2O$ unaccounted for.
						Uncorrected.	Corrected.*	
	grams.	grams.	grams.	grams.	milligrams.	cubic centim.	cubic centim.	
20	—	1.5822	1.57945	1.57325	6.2	2.65	2.55*	0.044
21	2.71828	1.7413	1.73836	1.73130	7.06	2.95	2.85*	0.050
22	4.7325	—	3.0258	2.9928	33.0	16.36	[15.86*?]	[0.030?]
23	2.01084	1.2880	1.2856	1.2504	35.2	—	—	—
24	7.211	—	4.6075	4.6055	2.0	0.33	0.32*	0.019
25	3.979	—	2.5443	2.5403	4.0	0.93	0.90*	0.055
Total Average								0.040
Average omitting 22								0.042

The filtrates from the precipitates of basic salt did not deposit any further solid upon long standing. That from the last determination was rendered very distinctly acid to methyl orange by the addition of a milligram of sulphuric acid, in spite of the difficulty in detecting the color-change in the presence of the blue cupric sulphate. These tests indicate that the filtrate was wholly normal.

In order to test still more definitely the accuracy of the method, the following mode of procedure was devised. To neutral solutions of cupric sulphate — prepared either from the purest crystals or by long standing after the neutralization of the trace of acid in ordinary "chemically pure" material — were added small measured amounts of a standard sodic hydroxide solution. After a time, the precipitate was filtered off and dissolved in standard sulphuric acid, exactly as if it had been obtained by the expulsion of the acid through heat.

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* See page 266, Experiments 26–37.

TEST OF METHOD.

Precipitation and Solution of Basic Cupric Sulphate.

Number of Experiment.	Concentration of Solution.	Time between Precipitation and Filtration.	Twentieth normal NaOH used.	Twentieth normal H_2SO_4 used.	Factor $= \frac{c.\ c\ NaOH}{c\ c.\ H_2SO_4}$
			cub centim.	cub centim.	
26	Strong.	10 minutes.	3.00	2.85	1.05
27	Strong.	90 minutes.	3.00	2.94	1.02
28	Medium.	15 hours.	3.00	3.14	.95
29	Dilute.	1 hour.	6.00	6.24	.96
30	"	90 minutes.	6.00	6 27	.95
31	"	" "	3.00	3.12	.96
32	"	" "	3.00	3.14	.95
33	"	" "	3.00	3.03	.99
Average of Experiments 28–33					0.96

It is hence evident that from dilute solutions the basic salt is wholly precipitated in a comparatively short time. Even under the worst conditions no deficiency approaching that noticed in Experiment 25 was observed. Another series (Experiments 34–37), made in very dilute solutions without filtering, gave values for the factor which respectively equalled 0.97, 0.98, 0.95, and 0.98. The average is 0.97, not seriously different from that found above. The first value of the factor was used in correcting the results of Experiments 20–25. The correction involved is extremely slight except in Experiment 22, where the application of the full value of the factor to a very large quantity is of doubtful advisability. Hence it is better to omit this experiment from the final average.

One contingency alone is not provided for by these test experiments that is to say, the formation of a cuprous compound and its solution in the cupric salt. The formation of a cuprous salt by gentle ignition of cupric sulphate in the air is far from probable; but for fear that such a reaction had taken place, the solution of the cupric sulphate was usually exposed to the air from twelve to twenty-four hours before filtration. The fact that exposure to the air for a long time after filtration caused no further formation of precipitate is a satisfactory proof that no cuprous salt remained in solution, even if it had been formed in the first place.

The outcome of all these more or less indirect experiments points to the conclusion that cupric sulphate retains about 0.12 per cent of its water of crystallization, even when heated to 400° C. This last trace of water is given off only at a temperature at which the cupric sulphate itself begins to decompose. It must be admitted that the evidence upon the point is not absolutely certain, but there is no doubt of its great probability. Upon such a matter as this it is difficult to see how more definite results could have been procured.

Total Percentage Composition of $CuSO_4 . 5 H_2O$.

		Per Cent.
Water lost at 360° — 400°	=	36.067
" " between 400° and redness	=	0.042
Copper, average	=	25.449
SO_4	=	38.436
Total	=	99.994

If the amounts of copper and sulphuric acid supposed to be lost during the electrolysis are added, the total becomes 100.004.

Either of these total results is now accurate within the limits of error of ordinary analysis. But it will be seen that the total percentage of crystal water indicated by the analyses is much too large as compared with the sulphuric acid, which is our only certain standard of reference. This excess of water must have been occluded in the original crystals, which were not very finely powdered. Accordingly two specimens of the purest cupric sulphate were much more finely pulverized, and their loss of weight at 400° was then found to be 36.057 (average of Experiments 21 and 23) instead of 36.067 per cent. Mr. H. M. Richards kindly measured many diameters in the two powders, and found that the particles of the coarser powder approximated one tenth of a millimeter, while those of the finer were less than one hundredth. Since more than half an hour's continuous powdering, at the very slow rate adopted to prevent warmth from friction, had been necessary to reduce a small amount of material to the finer state, it was concluded to abandon the attempt at obtaining cupric sulphate free from occluded water.

It must be remembered that the salt had been very slowly crystallized by the evaporation of the solution, and of course had had every opportunity to imprison traces of the mother liquor. Crystallization from hot solutions could not be adopted because of the risk of the formation of basic salt.* But even if the true amount of the water of crystallization could have been determined, it would have been of little present use for the determination of the atomic weight of copper, because of the uncertainty in its molecular weight. It is hoped that an investigation of the quantitative relations of water in other compounds may be in progress during the coming year at this Laboratory.

The Atomic Weight of Sulphur.

It is seen that the ratio between the weights of sodic carbonate and sodic sulphate found in each analysis of cupric sulphate forms a valuable check upon the purity of the first substance. Conversely, if we assume the purity of each of the substances and the molecular weight of one of them, we obtain data for calculating the molecular weight of the other. Since sulphur is probably the least definitely determined of the elements involved, the figures may be used with advantage for the calculation of its atomic weight.

MOLECULAR WEIGHT OF SODIC SULPHATE.

Weights reduced to Vacuum.

No. of Experiment.	Source of Acid.	Na_2CO_3 taken.	Indicator.	Na_2SO_4 found.	Molecular Weight Na_2SO_4 if Na_2CO_3 = 106 108.
		grams.		grams.	
4	Electrolysis	1.29930	M. O.	1.74113	142.189
6	"	3.18620	Av.	4.26790	142.131
11	Distillation	1.01750	M. O.	1.36330	142.169
12	"	2.07680	M. O.	2.78260	142.169
7	Electrolysis	1.22427	Av.	1.63994	142.133
17	Distillation	1.77953	Phth.	2.38465	142.189
17	Electrolysis	2.04412	Phth.	2.73920	142.189
38	Distillation	3.06140	Phth.	4.10220	142.180
Average Molecular Weight of Na_2SO_4					142.169
Average omitting Experiments 4, 6, and 7, which are less reliable than the others					142.181

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* Hampe, *loc. cit.*

The first column of this table indicates the original number of the experiment. The data of Experiments 17 and 38 are given for the first time. The second column shows the source of the acid. The third column gives the weights of sodic carbonate taken; while in the fourth are recorded the indicators used in determining these weights, the abbreviations standing for methyl orange, phenol phthaleïn, or the average of the two. The last two columns contain respectively the weight in grams and the molecular weight of the sodic sulphate. Since half of the results were obtained with methyl orange, it is unnecessary to correct the result for the trace of impurity in the sodic carbonate.

Subtracting from the averages the quantity $Na_2O_4 = 110.106$ we obtain two values for the atomic weight of sulphur: —

From the first average,	$S = 32.063$
" second average,	$S = 32.075$
Usually accepted value,	$S = 32.06$

A large alteration in the assumed atomic weight of sodium would of course make very little difference in the result, while an alteration of $\frac{1}{1000}$ of its value in the atomic weight of carbon changes the atomic weight of sulphur by only about the twentieth of one per cent. Although it is certain that the results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur, the outcome of the comparison is nevertheless an interesting check upon the work previously described.

The check just mentioned proves that the sodic carbonate contained the normal amount of carbon dioxide, but does not prove the absence of a very small amount of neutral impurity from the salt. Such impurity would have but a slight effect upon the ratio of the weights of the two compounds. It is true that this effect would be to diminish instead of to increase the observed atomic weight of sulphur; but it was thought advantageous to attempt the comparison of the sodic carbonate with some salt having a very different equivalent weight, in order to obtain more light upon this point. Accordingly the material to be investigated was converted with suitable precautions into sodic bromide. In Experiment 39, 1.2198 grams (in vacuum) of sodic carbonate yielded 2.3685 grams (in vacuum) of the bromide; or $2\ NaBr : Na_2CO_3 = 206.022 : 106.103$. Upon its face the result was very satisfactory, but the great hygroscopic power of sodic bromide and various other complications afforded a wide possibility of error; hence the experiment was not repeated. To be of value, any such determination must be made the subject of an especial investigation; and for this, with so remote a purpose as the present one, time was wanting.

The Atomic Weight of Copper.

The calculation of the atomic weight of copper from the amount of metal contained in cupric sulphate which has been dried at 250–270° gives the value 63.35. This result sufficiently approaches Hampe's (63.32) to show the identity of the materials used. But it has been proved that such cupric sulphate still contains a comparatively large amount of water; and this fact renders useless the careful analyses made in 1874. The effect of the correction is considered in a following paragraph.

Besides this method of calculation "from difference," the data which have been given afford twelve other ratios for the computation of the atomic weight of copper. Six of these ratios are useless because of the known error in the crystal water; namely, $5\,H_2O : Cu$; — $SO_4 . 5\,H_2O : Cu$; — $5\,H_2O : CuSO_4$; — $Na_2CO_3 : CuSO_4 . 5\,H_2O$; — $Na_2SO_4 : CuSO_4 . 5\,H_2O$; — and $BaSO_4 : CuSO_4 . 5\,H_2O$. Three of these last ratios give values which are much too low, and the other three give values which are much too high, as would naturally be expected. The mean is curiously near to the true value, but need not be further discussed. Neglecting these results because of the known constant error which vitiates them, there still exist seven ratios which do not involve the uncertain amount of the water of crystallization.

I. From calculation based upon the results tabulated on page 267 anhydrous cupric sulphate is seen to contain certainly over 39.807 per cent of copper, and very probably as much as 39.832 per cent. The first number gives 63.53 as the atomic weight of copper, and this value must be regarded as the lowest possible limit. The second much more probable figure, which takes into account the water held by cupric sulphate at 400°, gives the proportion:

$$(CuSO_4 - Cu) : Cu = (100.000 - 39.832) : 39.832 = 96.06 : \mathbf{63.593}.$$

II. From Experiments 4, 6, 7, and 8 it is found that 7.2501 grams of sodic carbonate correspond to 4.34583 grams of copper when methyl orange is used as an indicator; and from Experiments 6, 7, and 8 it is found that 5.95165 grams of sodic carbonate correspond to 3.56697 grams of copper when phenol phthalein is used as an indicator. It has been shown that the impurities of the sodic carbonate probably rendered the latter quantity of the salt about 0.007 per cent too high; hence the true weight should have been 5.95123. The correction is so small that it has not heretofore been applied.

From these values we obtain the proportions:

$$\begin{aligned} Na_2CO_3 : Cu &= 7.25010 : 4.34583 = 106.108 : 63.603 \\ &= 5.95123 : 3.56697 = 106.108 : 63.597 \\ &\text{Average} \qquad \mathbf{63.600} \end{aligned}$$

The highest individual result was 63.604, the lowest 63.592, when entirely uncorrected.

III. From Experiments 4, 6, 7, and 9 it is apparent that 10.95552 grams of sodic sulphate are equivalent to 4.90165 grams of electrolytic copper. Hence:

$$Na_2SO_4 : Cu = 10.9555 : 4.90165 = 142.166 : \mathbf{63.607}.$$

Highest value 63.614
Lowest " 63.595

The last determination (Experiment 9) is by far the most trustworthy. The value deduced from it is 63.600.

IV. From Experiments 4 and 6 it is evident that 4.4855 grams of sodic carbonate (average) are equivalent to 6.75463 grams of cupric sulphate which has been dried at 360°. But it is reasonably certain that this cupric sulphate still contained sixty-six hundred-thousandths of its weight of water. Making the appropriate correction we have:

$$\begin{aligned} Na_2CO_3 : CuSO_4 = 4.4855 : (6.7546 - .0044 = 6.7502) \\ = 106.108 : 159.681 \end{aligned}$$

Highest value 159.703
Lowest " 159.673

Subtracting $SO_4 = 96.060$, the average value $Cu = \mathbf{63.621}$ is obtained.

V. In the same way, from Experiments 4, 6, and 9, 9.31558 grams of sodic sulphate are seen to correspond with $10.4715 - 0.0069 = 10.4646$ grams of really anhydrous cupric sulphate. Hence:

$$Na_2SO_4 : CuSO_4 = 9.3156 : 10.4646 = 142.166 : 159.701$$

Highest = 159.73
Lowest = 159.65

From the average, $Cu = \mathbf{63.641}$. This result has a very large probable error, in the chemical as well as in the mathematical sense.

VI. and VII. Only one experiment was made with baric sulphate, but the result is appended for the sake of completeness. From No. 10 it is seen that 100.000 parts of crystallized cupric sulphate are equivalent to 93.289 parts of baric sulphate. But the same amount of the same specimen of the salt had been shown to contain 25.448 parts of copper and 36.109 parts of water. (See pages 260 and 267.) From these data: —

VI. $BaSO_4 : Cu = 93.289 : 25.448 = 233.16 : \mathbf{63.603}$
VII. $BaSO_4 : CuSO_4 = 93.289 : 63.891 = 233.16 : 159.685$

From the last value Cu = **63.625**. The atomic weight of barium probably lies between 137.0 and 137.2; the mean value is assumed above. The corresponding variations of the atomic weight of copper would be from 63.57 to 63.63 with the first ratio, and from 63.54 to 63.69 with the second.

The results of the seven ratios dependent upon the analysis of cupric sulphate are collected in the following table.

THE ATOMIC WEIGHT OF COPPER.

	Ratio.	Lowest.	Highest.	Experimental Mean.
I.	$(CuSO_4 - Cu) : Cu$	[63.53]	[63.62]	63.593
II.	$Na_2CO_3 : Cu$	63.592	63.604	63.600
III.	$Na_2SO_4 : Cu$	63.59	63.61	63.607
IV.	$Na_2CO_3 : CuSO_4$	63.61	63.64	63.621
V.	$Na_2SO_4 : CuSO_4$	63.59	63.67	63.641
VI.	$BaSO_4 : Cu$	[63.57]	[63.63]	63.603
VII.	$BaSO_4 : CuSO_4$	[63.54]	[63 69]	63.625
Average				63 612
Average, omitting V. and VII. for obvious reasons . .				63.605

The correction of the experimental mean, in each case, for the amount of copper and sulphuric acid lost during electrolysis, diminishes the variations noticeable above to a remarkable degree. But since the validity of this correction is doubtful, and since its application scarcely influences the two most important results (II. and III.), the figures have been allowed to stand uncorrected. The final average would have remained essentially the same. The highest and lowest values given in this table are in several cases much more seriously in error than the actual experimental results. The reasons for this widening of the limits will be sufficiently understood through a careful perusal of the matter which immediately precedes the table.

Changes in the atomic weights of the elements used as standards of reference of course cause slight changes in the corresponding atomic weights of copper. Sulphur enters into a larger number of the ratios than any other element, excepting of course oxygen and copper; but a reasonable change in its assumed atomic weight, while slightly affecting individual results, has no effect upon either of the averages. Carbon and sodium are both determined with a high degree of accuracy, and oxygen is our standard of reference. A fuller discussion of these results will be found in the concluding summary.

II. Synthesis of Cupric Sulphate.

Parallel with the experiments which have just been described was commenced a series of syntheses of cupric sulphate. It was hoped that the results might furnish a valuable confirmation to the conclusions based upon the analytical work, but the outcome of the series was very disappointing.

The method of experiment was as follows. A weighed amount of pure electrolytic copper,* which had been ignited in hydrogen, was dissolved in the purest nitric acid in a platinum flask provided with bulb tubes for the condensation of spray. A slight excess of pure sulphuric acid was then added, and the whole was evaporated to small bulk in a platinum dish. After transferring to a small crucible enclosed in a larger one, the remaining solution was evaporated to dryness on the steam bath; and the residue was gradually raised to a temperature of 400°. After some time the crucible was quickly covered, placed in a phosphoric oxide desiccator, and allowed to cool in a vacuum. Air having been admitted through suitable drying tubes, the crucible was quickly weighed. The product of the experiment soon reached constant weight upon reheating, but it was invariably found to contain a very perceptible amount of imprisoned sulphuric acid, which rendered its solution strongly acid to methyl orange. It is evident from the preceding section that this impurity is

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* For mode of preparation, see these Proceedings, XXV. 199, 206.

not retained when pure sulphuric acid is added to powdered cupric sulphate which has already been nearly dehydrated, but only when the salt is crystallized from strongly acid solutions. This fact rendered the present experiments useless for their original purpose. The results of the two determinations show how insidious constant error may be, if not guarded against by check experiments.

SYNTHESIS OF CUPRIC SULPHATE FROM METALLIC COPPER.

*Weights reduced to Vacuum.**

Number of Experiment.	Metallic Copper taken.	Cupric Sulphate found.	Per Cent of Copper in Cupric Sulphate.
	grams.	grams.	
40	0.67720	1.7021	39.786
41	1.00613	2.5292	39 781
Average			39.784
From Analysis of Cupric Sulphate dried at 400° . .			39.807

In order to show that the large difference between these two averages was due solely to the occlusion of sulphuric acid, the following experiment (No. 42) was made. 3.1227 grams (in vacuum) of the purest crystallized cupric sulphate were dried at 400°, the residue weighing 1.9963 grams. The nearly anhydrous salt was then carefully dissolved in water, and after the addition of small quantities of nitric and sulphuric acids it was evaporated and ignited at a temperature even somewhat higher than before. A gain of 0.0013 gram was apparent, very nearly corresponding to the difference noted above. The acids, tested immediately afterwards, left no weighable residue upon evaporation.

While it was apparent that these experiments were useless for their original purpose, it was hoped that their comparison with similar syntheses from cupric oxide might furnish valuable indirect evidence with regard to the quantitative relations of the latter important substance. The hope was not in vain.

The cupric oxide used as the basis of the three following experiments was prepared essentially in the manner described in these Proceedings, Volume XXV., page 199. The three experiments represent

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* Specific gravity of Cu = 8.95; of $CuSO_4$ (Hampe and Karsten) = 3.61.

as many different preparations, in making which various different precautions were observed; but in a paper already far too prolix the omission of these minor points will be well pardoned. The cupric oxide was ignited to constant weight at a dull red heat in a double crucible, and cooled in a vacuum as usual. The outside crucible was of platinum in the second and third experiments, and in these cases the inner crucible was observed to have gained noticeably in weight during the ignition. The last weight was adopted, for obvious reasons. In the first and last cases the solution of the oxide was conducted in the crucible, without transferring, while in the second experiment the cupric oxide was dissolved in the platinum flask with bulb tubes. In each case both nitric and sulphuric acids were added, that the conditions might be similar to those of the preceding syntheses. The cupric sulphate used by Baubigny in his analyses was prepared in a somewhat similar way, and hence in this respect his result is comparable with these.

SYNTHESIS OF CUPRIC SULPHATE FROM CUPRIC OXIDE.

Weights reduced to Vacuum.[*]

Number of Experiment.	Cupric Oxide taken.	Cupric Sulphate found.	Per Cent Cupric Oxide in Cupric Sulphate.
	grams.	grams.	
43	1.0084	2.0235	49.835
44	2.7292	5.4770	49.830
45	1.0144	2.0350	49.848
		Average	49.838
Theory if Cu = 63.6			49.856
" " = 63.34			49.774
Baubigny's result			49.815

The comparatively close agreement between the average and the theory is solely due to an elimination of opposite errors. This fact will be more evident in the following section.

In order to show that no material was mechanically lost during the syntheses, the last sample of cupric sulphate from each of the two series was electrolyzed. The result of one of these electrolyses has

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[*] Specific gravity of CuO = 6.3; of $CuSO_4$ = 3.61.

already been given in Experiment 16; the other yielded 0.8096 gram of metal from 2.0350 grams of the sulphate, or 39.78 per cent of copper.

It is evident that impure cupric sulphate prepared in this manner contains about 39.784 per cent of copper and about 49.838 per cent of ordinary cupric oxide. That is to say, 39.784 parts of copper correspond to 10.054 parts of the remainder of cupric oxide. Assuming this remainder to consist solely of oxygen, the atomic weight of copper would be 63.312. But upon comparing the quantity 10.054 with the quantity of sulphuric anhydride found by difference, 50.162, it is evident that a grave error exists in the former figure. This error becomes only more apparent when allowance is made for the occluded acid.

These inferences are based upon data of somewhat uncertain accuracy, it is true; but the error is nevertheless so large as to be apparent even to cruder analysis than this. The full explanation of the results, as well as of the variation exhibited by Baubigny's analysis, must be deferred to the next section. The doubts raised by the data under discussion formed a useful introduction to the study of cupric oxide.

III. The Analysis of Cupric Oxide.

Deprived of the support of the results from cupric sulphate, Hampe's oxide determinations possess little more weight than those of any other experimenter. It will be remembered that the values of the atomic weight of copper deduced from this source have varied from 63.1 to 63.5. Such a fluctuation alone, without the confirmatory evidence which has just been given, is sufficient to cause the suspicion of an undiscovered error in cupric oxide.

With the hope of detecting the possible error, a number of analyses of the substance were made under varying conditions and with different samples of material. No difficulty was found in obtaining results varying as widely as those cited above. Part of the cause of this variation was traced to differences in the preparation, and part to differences in the temperature and tension of the surrounding air employed in ignition.* Cupric oxide ignited to constant weight at a very dull red heat lost a very perceptible amount of material upon

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* Compare Bailey and Hopkins, J. Ch. Soc. Trans., 1890, p. 269. Also Schutzenberger, quoted in Am. J. Sc., [3], XXVI. 65.

heating to the highest temperatures which hard glass would bear. On the other hand, copper reduced by hydrogen at the lowest possible temperatures is well known to lose in weight on heating to bright redness. Some of Erdmann and Marchand's experiments[*] show that the exhaustion of the tube at the time of weighing makes very little if any variation in the weight of the materials; but from others,[†] as well as from the fiftieth experiment below, it would appear that exhaustion at the time of ignition introduces a somewhat more serious correction. In this last case the apparatus was necessarily rather complicated, to admit of the ignition and weighing of the copper and its oxide in a Sprengel vacuum, but the full description of the contrivance would demand more space than it is worth. In the four preceding experiments Hampe's method was carefully followed.

The mode of preparation of the cupric oxide was essentially that recommended by Hampe, and described in these Proceedings, Volume XXV., page 199. In some cases the basic nitrate was not washed with water before ignition, and in other cases it was thus washed. In general, none but platinum vessels were used. Various slight unimportant modifications were introduced, which need not find a place here. The essential conditions to be borne in mind are the invariable use of the nitrate as the source of the oxide, and the variable temperatures employed in the ignition.

ANALYSIS OF CUPRIC OXIDE.

Weights reduced to Vacuum Standard.

No. of Exp't.	CuO dull redness 550°±	CuO 750°?	Cu found 400°±.	Cu found 550°±.	Cu found 750°?	Atomic Weight of Copper $O : Cu = 16 : x$.
	grams.	grams.	grams.	grams.	grams.	
46	2.08491	—	—	1.66405	—	63.26
47	1.11936	1.11851	—	0.89355	—	63.29 to 63.53
48	1.06300	1.06253	[0.8490]	—	0.84831	63.23 to [63.62]
49	1.91703	1.91656	—	—	1.5298	63.20 to 63.29
50	2.62410	Ignited	in vacuum	2.0956	—	63.44
[General Average						63.37]

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[*] *Loc. cit.* (see p. 241).

[†] J. prakt. Chem., XXVI. 461.

The average of results so heterogenous in nature can naturally have no important meaning, but it is interesting to note the approximation to the old value of the atomic weight. The high value given in Experiment 48 is manifestly only a compensation of errors. From Experiments 48 and 49, the only two in which both materials were ignited at a bright red heat, 2.97909 grams of cupric oxide yielded 2.37811 grams of metallic copper. Computing from these data the atomic weight of copper, we obtain the value 63.313, which is comparable with the result 63.312 obtained indirectly through the synthesis of the sulphate as well as with the number 63.346 fixed upon by Hampe. The absolute identity of the first two figures must be attributed to chance, since the agreement of the individual results was not perfect.

These results again pointed to the existence of a volatile impurity in cupric oxide, but no proof was afforded that the impurity was wholly driven off at the temperature of fairly bright redness. The determination of this point, as well as of the nature of the occluded material, became a matter of great importance.

Tests for Impurities.

The first hypothesis suggested was the possible imprisonment of a small amount of water.[*] To subject this hypothesis to proof, pure cupric oxide might be dried at a red heat, and reduced by means of carbon monoxide, when of course any occluded water would be set free and might be weighed.

The cupric oxide used in the execution of this plan was some of that which remained from the oxygen research. It had been prepared in the usual manner. The carbon monoxide was made from oxalic and sulphuric acids, and after a preliminary purification with caustic potash the gas was collected over water in a glass gasholder. From this receptacle it was passed through very large amounts of potassic hydroxide, over calcic chloride and red hot platinum sponge, and finally through a flask containing sulphuric acid and two tubes containing phosphorus pentoxide, before being allowed to come in contact with the material to be reduced.

In Experiment 53, — which may be taken as a type, — fifteen grams of the cupric oxide contained in a hard glass tube were dried at a red heat in a stream of pure air for forty-five minutes. A small weighed phosphoric oxide tube was then connected at the exit, and the current of air was continued for over an hour.

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[*] See Müller-Erzbach, Jahresbericht, 1885, p. 74.

Grams.
Weight of tube before connection = 55.1920
" " after " = 55.1922

The temperature changed from 15°.7 to 16°.8 between the two weighings, involving a correction of —.0001 to the latter weight. The tube therefore gained only the tenth of a milligram, showing the cupric oxide to have reached a constant hygroscopic condition.

During the ensuing reduction with carbon monoxide, the drying tube was again connected with the apparatus. Before the last weighing of the tube, all carbon dioxide was expelled by pure air. The tube weighed 55.2177 grams, showing a gain of 0.0255 gram, or 0.017 per cent of the weight of the cupric oxide.

Two similar experiments led to like results.

REDUCTION OF CUPRIC OXIDE BY CARBON MONOXIDE.

No. of Experiment.	CuO taken.	Water formed.	Volume of Carbon Monoxide.	Weight of H_2O for 10 grams CuO.
	grams.	grams.	litres.	grams.
51	6.90	.0105	—	.0152
52	20.00	.0347	—	.0173
53	15.00	.0255	5.5	.0170

Nothing in these results proved that the water was not formed from the oxidation of hydrogen or hydrocarbons possibly contained in the carbon monoxide, and indeed further examination showed that it originated from this source. The metallic copper from the last experiment was immediately oxidized by a stream of pure dry air, and once more reduced with carbon monoxide. Four litres of gas required to reduce the partially reoxidized copper yielded 19.3 milligrams of water. Since this water could not possibly have come from the oxidized copper, it must have been solely obtained from impurities in the carbon monoxide. The quantity closely agreed with the amount, 18.3 milligrams, which one would have expected to find from the volume of gas used, upon the basis of previous results. Considering the fact that the volumes of gas were not very accurately measured, the difference is not greater than the experimental error. Hence it may be safely concluded that the carbon monoxide contained about four one-hundredths of a per cent of hydrogen by weight, but that the *cupric oxide retained no appreciable amount of water at a red heat.*

Experiments 54 *and* 55. — The idea that some cupric nitrate might remain undecomposed in cupric oxide is evidently not a new one, for almost every experimenter upon the subject tested for nitric acid in the water formed during the reduction. It seemed possible, however, that the nitric acid might be reduced as well as the cupric oxide, and hence that the test might not be a sufficient criterion. Accordingly, five grams of cupric oxide were dissolved in very pure dilute sulphuric acid, and several successive portions of water were distilled off from the mixture. After evaporation to small bulk in a platinum dish, the distillates were found to be neutral to methyl orange and acid to phenol phthalein. When the amount of standard alkali necessary to neutralize this acidity had been determined, hydrochloric acid was added and the sulphuric acid present was estimated as baric sulphate. Since the weight of baric sulphate (3.7 mg.) was nearly equivalent to the amount of alkali used (0.39 c. c. of a decinormal solution), since no nitric acid was found in the filtrate by the most sensitive tests, and since a very perceptible amount of copper was found there, it may be reasonably concluded that cupric sulphate had been carried over mechanically in fine drops. A second experiment yielded like results. Hence, so far as this test was concerned, *no nitric acid was to be found in cupric oxide.*

Experiment 56. — The tendency of various oxides to hold carbonic acid even at high temperatures is well known. Thudichum * has observed that, in order wholly to free cupric oxide from this impurity, it is necessary to ignite it in a vacuum. In order to test this point so far as it concerns the present investigation, the following experiment was made. After a small amount of nitric acid had been added to twelve grams of cupric oxide, the substance was gradually brought to redness and maintained at this temperature for ninety minutes. The material was then rapidly transferred to a flask provided with a stoppered funnel and two bent tubes. One of the latter was connected with two test tubes containing a clear solution of baric hydroxide, and the other permitted a gentle current of air to be blown through the entire apparatus. Before either baric hydroxide or cupric oxide were added, all the tubes and flasks were of course freed from carbon dioxide. Finally, dilute boiled hydrochloric acid was run in at the funnel tube, the cupric oxide was dissolved, and the solution was gradually brought to boiling. A slight bluish precipitate of cupric hydroxide appeared after some time in the first test tube, while the

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* Chem. Soc. Journ., 1876, [2], p. 364.

second remained perfectly clear. The excess of baric hydroxide in the first tube was quickly neutralized with weak hydrochloric acid and phenol phthalein, and the precipitate was filtered off and washed. The absence of barium from this precipitate proved the absence of carbon dioxide from the cupric oxide.

In order to test the adequacy of the method, 3.4 milligrams of sodic carbonate were added to the cupric chloride through the funnel tube. This quantity yielded only one tenth the amount of carbon dioxide necessary to account for the difference between the atomic weights of copper in question, but it nevertheless produced a heavy white precipitate in both newly filled baric hydroxide tubes. The precipitate when tested showed large quantities of barium; hence the method was quite competent to decide that *the absorption of carbonic acid by cupric oxide was not the error for which search was being made.*

Experiment 57. — Although it seemed very improbable that cupric oxide could contain even traces of a higher oxide after ignition at a red heat, proof of the point was not at hand. Accordingly, four grams of the substance were boiled with pure hydrochloric acid in an apparatus somewhat resembling the last one, in which all the joints were of sealed or ground glass. The vapors were driven through a reversed air cooler into bulbs containing a strong cooled solution of potassic iodide. The very small amount of iodine set free after some time was determined by means of sodic thiosulphate. This amount corresponded to 0.05 milligram of oxygen but even this was undoubtedly due to copper in uncondensed spray. Eight tenths of a milligram of potassic dichromate, subsequently added to the cupric chloride, at once set free more than double this amount of halogen in the bulbs. The method was hence shown to be adequate for the purpose. The results *prove the absence of an essential amount of any higher oxide or oxidized nitrogen from ordinary cupric oxide.*

The Determination of Occluded Gases.

After so much negative evidence, the only remaining hypothesis which could account for the irregularity of the atomic weight of copper deduced from cupric oxide is that of the occlusion of gases by the substance. This idea is by no means new. As long ago as 1842 Erdmann and Marchand* showed that at least a small amount of air

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* J. f. prakt. Chem., XXVI. 461.

was condensed by the substance. Frankland and Armstrong* found in 1868 that cupric oxide prepared from the nitrate contains both carbonic acid and nitrogen. Hilditch† states that oxygen gas is occluded by cupric oxide at a red heat, and estimates the effect of this impurity upon the atomic weight of oxygen, without, however, adducing any experimental data. More recently Morley‡ has found that cupric oxide slowly gives off a gas in vacuum. It is a noticeable fact that cupric oxide is almost as serviceable as platinum in preventing bumping during ebullition.

The simplest and surest method for the liberation of an occluded gas is completely to dissolve the cupric oxide in a pure acid. It is by no means certain that indefinite heating in a vacuum would accomplish the end in view. Several pieces of apparatus more or less suitable for the present purpose were devised in succession, and by their means it was proved that some varieties of cupric oxide occlude important quantities of aeriform material. Nearly fifty determinations were made.

According to the first method a tube of the shape shown in Figure 1 was filled at the end with freshly ignited cupric oxide, and in the middle with pure boiled sulphuric acid. When the whole had been completely exhausted by means of a Sprengel pump, the liquid was allowed to come in contact with the solid, and the gas evidently set free was pumped out and measured. But the action was of course only a very superficial one, and no amount of long standing or violent shaking could accomplish a more complete change. Three experiments indicated that at least a small amount of gas, which appeared to be chiefly nitrogen, was set free. Since it was difficult to decide how much cupric oxide had been combined, the method was abandoned.

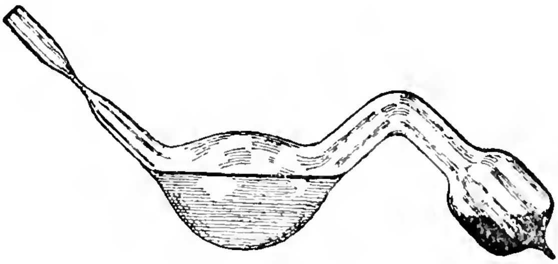

FIG. 1.

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* Chem. Soc. Journ., XXI. 89, 93 (1868).

† Chem. News, XLIX. 37 (1884).

‡ Am. J. Sci., XLI. 231, March, 1891.

Subsequently, more dilute boiled sulphuric acid was used; and the apparatus was sealed by fusion after exhausting, but before mixing the acid and base. The mixture was digested upon the water bath until the action was nearly or quite completed. It was found that this completion was greatly facilitated by violent shaking at the moment when the acid was poured upon the cupric oxide, for otherwise the materials inevitably formed a hard cake which dissolved very slowly. In one or two cases a small amount of unchanged cupric oxide was weighed, and subtracted from the original amount.

The apparent evolution of gas was at first very violent; but this violence might have been partly due to ebullition caused by the heat of the chemical action. The tubes were opened under boiled water or mercury, and the gas was analyzed by means of Hempel's apparatus, somewhat modified for accurate use with very small quantities of material. The portion of the gas which was not absorbed by caustic potash, but was absorbed by pyrogallol, is tabulated below as oxygen. The remainder refused to support combustion, suffered no diminution of volume upon the addition of oxygen, and appeared perfectly inert; hence it was undoubtedly nitrogen. In order to test the solution of pyrogallol, analyses of air were made from time to time, with satisfactory results. The volumes were of course corrected for temperature and pressure, as well as for the tension of aqueous vapor, before the weights of gas were calculated. The conditions varied so little from the mean, 24° C. and 760 mm., that a statement of these data seems inessential.

The occlusion of an inert gas by cupric oxide was so peculiar a phenomenon that many experiments were needed to carry conviction. Several blank experiments were tried, in order to test the freedom of the acid from dissolved air. The fact that only a very small amount of gas was evolved in the second experiment is also valuable evidence upon this point.

The material used in Experiments 58, 63, and 64 was four years old, while that used in Experiments 59, 65, 66, and 67 had been recently prepared. Both of these samples were made from cupric oxynitrate, whereas the one used in Experiment 61 was precipitated by caustic alkali. The tubes of Nos. 64 and 67 were opened under mercury. In No. 64 the cupric oxide was cooled for forty-eight hours after igniting, while in No. 66 the oxide was still very hot when introduced into the tube.

Occluded Gas in Cupric Oxide. — First Series.

No. of Experiment.	Weight of Cupric Oxide.	Vessel employed for Ignition.	Temperature of Ignition.	Vol. of Gas evolved uncorrected.	Vol of O_2 for 1 grm. of CuO.	Vol. of N_2 for 1 grm of CuO.	Per Cent of Gas in CuO by Weight.
	grams.			cub. cent.	cub. cent.	cub. cent.	
58	4.35	Porcelain	Dull red	2.70	0.03	0.59	0.075
59	3.12	Double xble Platinum	Bright red	0.30	0.01	0.09	0.012
60	Blank	—	—	0.10	—	—	—
61	1.20	—	Not ignited	3.5 of CO_2	Trace	Trace	
62	Blank	—	—	0.10	—	—	—
63	1.20	Porcelain	Dull red	0.73	0.03	0.58	0.073
64	2.20	"	"	1.34	0.03	0.58	0.073
65	2.00	"	"	0.8±	Trace	0.40	0.05±
66	3.20	Double xble Platinum	"	1.70	0.05	0.48	0.064
67	2.10	Porcelain	"	1.13	0.00	0.53	0.065

The series was discontinued because a new method had been devised which was much less tedious and much more direct in its execution. According to the new method, the cupric oxide to be analyzed was introduced into a tube shaped in the manner shown in Figure 2.

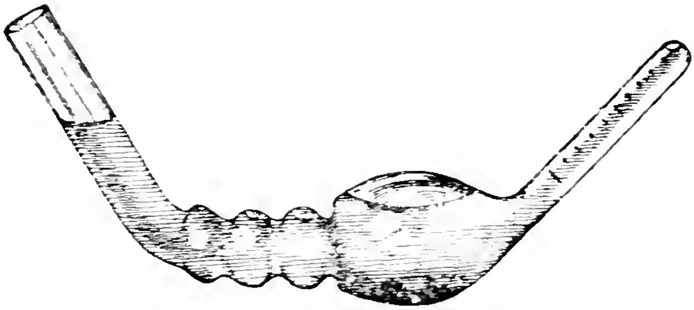

Fig. 2.

After the bulbs had been nearly filled with thoroughly boiled warm water, the open mouth of the tube was connected with an air pump to remove any mechanically adhering air. The water was usually allowed to boil for several minutes under the reduced pressure. The air was then readmitted, and the tube was entirely filled with pure boiled water, being placed perpendicularly for the purpose. When the tube had been returned to its usual position, acid was added through a fine funnel tube in such a manner that it at once attacked the oxide. A short piece of glass rod in the large bulb together with constant agitation prevented the formation of cakes.

In the most carefully performed experiments the sulphuric acid as well as the water was boiled, but repeated trials showed this precaution to be unnecessary. In one blank experiment even ordinary distilled water and sulphuric acid evolved only about one thousandth of a cubic centimeter of gas, while boiled water, which was invariably used in the determinations, gave no trace even of the finest bubbles with unboiled sulphuric acid.

The gas evolved on the solution of the cupric oxide was collected chiefly in the largest bulb. The amount collected in the smaller bulbs decreased in proportion with the increase of distance from the first, and only a very small amount was lost through the open mouth. The gas was measured in the right hand graduated tube, or drawn off for analysis through a rubber connector attached at this end.

The apparatus was afterwards modified to avoid the slight loss through the open mouth. It then consisted of a small stoppered flask with two concentric funnel tubes, and a delivery tube closed with a rubber connector and a pinch cock. When the whole apparatus had been filled with boiled water through the larger funnel tube, the smaller one was filled with pure sulphuric acid and quickly placed inside the larger one. Upon inclining the flask, it is evident that the loss of minute bubbles must have been reduced to a minimum, while the small annular opening between the funnel tubes was quite sufficient to allow the escape of the displaced water. The gas was readily drawn off for analysis through the delivery tube, which just penetrated the smooth rubber stopper.

Many varieties of cupric oxide were examined. Material obtained from the carbonate, or by precipitation from the sulphate, evolved little or no gas, thus affording an admirable proof of the purity of the acid and water. Check experiments with such material were accordingly made from time to time. Other circumstances being equal, the purer the oxide, the more gas was evolved. Solid impurities, such as alkaline salts, seemed partially to prevent the occlusion.

The volumes of gas are given without any correction, the temperature and pressure remaining so nearly constant that the observations are not recorded. The following table is intended only as a basis of rough comparison. The gas was frequently analyzed, with results similar to those tabulated above. The results confirm those of the preceding series.

Occluded Gas in Cupric Oxide. — Second Series.

No. of Exp't.	Nature of Cupric Oxide.	Weight of CuO.	Heat and Time of Ignition.	Volume of Gas evolved.	Per Cent of Gas in CuO by Weight.	Remarks on Method.
		grams.		cubic centim.		
68	Blank exp't.	—	—	0.00	—	$H_2SO_4+H_2O$
69	" "	—	—	0.00	—	" "
70	Precipitated	1.00	Dull red	0 10	0.011	Bulbs.
71	"	1.60	"	0.20	0.013	"
72	From Carbonate	1.50	Dull red	0.07	0.006	Bulbs.
73	" "	2.00	Dull red exposed to air	0.10	0.006	"
74	Crude, of Commerce, contained Cuprous Oxide.	3.00	Not ignited	0.70	0.026	Bulbs.
75		8.00	Dull red	2.00	0.028	Flask.
76		7.00	Not ignited	2.00	0.032	Another sample.
77	From Carbonate	1.50	Dull red	0.05	0.003	Flask.
78	Six Experiments with CuO prepared by action of CuO on $Cu(NO_3)_2$ & subsequent ignition of basic nitrate	1.70	Very low	0.34	0.023	Flask.
79		3.20	Dull red, 3 hrs.	1.03	0.036	"
80		1.20	Dull red, 7 hrs.	0.25(?)	0.023(?)	"
81		1.70	Bright red	0.09	0.006	"
82		2.00	Dull red	0.26	0.015	Pump not used.
83		2.00	Dull red	0.73	0 041	Pump not used.
84	After Hampe's method	0.39	310°; 2 hours.	0.17	0.050	Bulbs.
85	" "	1.10	" "	0.30	0.035	"
86	" "	1.82	600°; 2 hours.	1.35	0.084	Flask.
87	" "	0.39	700°; ¼ hour.	0.30	0.087	Bulbs.
88	" "	0.50	600°; 1 hour.	0.33	0.077	"
89	" "	0.60	600°; 4 hours.	0 41	0.079	"
90	" "	0.61	" "	0.36	0.070	Used HCl.
91	" "	0.44	" "	0.29	0.079	Bulbs.
92	New preparation	2.00	700°; ¾ hour.	1.37	0.080	See below.
93	" "	2.98	600°; 2 hours.	2.12	0.082	Flask.
94	" "	0.98	See below.	0.75	0.088	See below.
95	" "	0.50	900°; 1 hour.	0.17	0.039	
96	From Carbonate prepared from Nitrate	0.65	600°; 1 hour.	0.09	0.016	
97		0.50	290°.	0.10	0.023	
98	From Carbonate of Commerce	1.00	600°; 1 hour.	0.10	0.011	
99		0.75	" "	0.03	0.004	
100	Wire form	1.00	—	0.01±	0.001±	Contained Cu_2O.

The higher temperatures recorded above are merely approximate guesses. 600° signifies a dull red heat, 700° a medium red heat, and 900° a very bright red heat. In Experiment 92 the oxide was heated at the highest temperature obtainable by a Berzelius spirit lamp. In No. 94 the material was heated for an hour and a half in the Berzelius lamp, and then for an hour in a glass tube under a stream of oxygen. The oxide was transferred while warm to the bulb apparatus. It evolved upon solution 0.088 per cent of gas, one eighth of which was oxygen. In the ninetieth experiment hydrochloric acid was used for the solution of the oxide.

The two series of determinations, which were perhaps more numerous than necessary, showed the following important facts: —

First, that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas. (Nos. 58, 63–67, 84–94.)

Second, that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed. (Nos. 59, 81, and 95.)

Third, that beyond a certain limit the time of ignition makes no important difference. (Nos. 86–91.)

Fourth, that the gas was not absorbed from the air on cooling. (Nos. 64, 65, 66, and others.)

Fifth, that specimens of cupric oxide prepared in different ways contained very different amounts of gas. It is a curious fact that material which has been heated only to 300° contained less gaseous nitrogen than that which had been ignited at a higher temperature. In this case the nitrogen may still have existed in the combined form. (Nos. 78, 79, 84, 85.)

An explanation for the observed phenomena must necessarily be hypothetical, and will not be attempted at present.

In order to find the direct connection between the loss of weight noticed upon heating cupric oxide and the quantity of gas retained by the substance, the following experiment was made.

Experiment 101. — Cupric oxide which had been heated to constant weight at dull redness was ignited at bright redness in a double platinum crucible.

		Grams.
Weight of platinum crucible	=	18.0889
" crucible + CuO, 2½ hours at dull redness	=	19.65852
" " " 4 hours more "	=	19.65846
After ignition at very bright redness (20 minutes)	=	19.6574
" " " " (50 m. more)	=	19.6571
Total loss of weight	=	.0014

One gram of this specimen was shown to contain 0.00081 gram of occluded gas before ignition, and 0.00039 gram afterward (Experiments 86 to 95). In the quantity taken above this difference corresponds to a loss of weight of nearly 0.0007 grams, or about half of that observed. The remainder of the loss may have been due to a partial reduction of the oxide. (Compare page 275.)

Experiment 102. — In order to discover if heating cupric oxide in a vacuum produced any important evolution of nitrogen, six grams of cupric oxide were dried in a glass tube with the greatest care, exactly after the manner of Hampe, and weighed in the air. One end of the tube was then sealed, the other was attached to a Sprengel pump, and the whole was heated to about 500° C. for half an hour. Upon sealing and weighing; the loss of weight was found to amount to 4.4 milligrams. The amount of air displaced was found by opening the tube under boiled water, which wholly filled it. The weight of water, reduced to 4°, was 3.48 grams, while the temperature and pressure of the air at the time of weighing the exhausted tube were respectively 24° C. and 754 mm. Hence the weight of displaced air must have equalled 4.1 milligrams, or only 0.0003 gram less than the loss of weight actually observed. Therefore the cupric oxide could not have lost more than 0.005% of its weight under the treatment described.* The moist cupric oxide yielded approximately the usual volume of nitrogen upon solution in acids; but no very accurate measurement was made.

It has been said that these experiments were intended only for rough comparison. Since it appeared possible to apply a corresponding correction to the atomic weight of copper deduced from the oxide, it became important to make a more accurate series of determinations. The cupric oxide used in these final experiments represented three different specimens, similar to or identical with those used in Nos. 43, 45, 48, and 49.

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* In Experiment 50 the temperature of ignition was somewhat higher.

Occluded Gas in Cupric Oxide. — Third Series.

Number of Experiment.	CuO taken.	Gas evolved. [Apparatus.]	Temperature of Gas.	Atmospheric Pressure.	Per Cent of Nitrogen in CuO by Weight.	Per Cent of Oxygen in CuO by Weight.
	grams.	cubic centimeters.	Centigrade.	millimeters.		
103	1.84	1.38 (bulbs)	25°	757	0.080	0.003
104	1.80	1.55 (flask)	22°	763	0.094	0.004
105	1.30	1.10 (bulbs)	24°	760	0.090	0.004
		Average			0.088	0.004

The cupric oxide of the last determination was ignited for three hours in a stream of air, and for twenty minutes in a stream of oxygen, at a medium red heat. It was impossible to determine whether the material had reached constant weight, for the hard glass tube in which the ignition was conducted was very much altered by the heat.

As might have been expected, the very pure cupric oxide employed in these experiments contained a slightly greater amount of occluded gas than the less carefully prepared material of the earlier experiments. Since the latest samples of material were precisely similar to those used in the quantitative analysis of cupric oxide, it is fitting that the latest correction should be applied to those quantitative results. The 2.97909 grams of cupric oxide used in Experiments 48 and 49 (page 277) must have contained 0.00276 gram of occluded gas. That is to say, 2.97633 grams of pure cupric oxide correspond to 2.37811 grams of metallic copper. The difference between these weights now really represents the weight of combined oxygen present. The atomic weight of copper upon this basis is easily found to be 63.605.

Correcting the indirect results from the synthesis of cupric sulphate in the same way (see page 276) the number 63.603 is obtained. Averaging this result with that immediately above, the value 63.604 is found as a mean of five determinations including two wholly distinct methods.

Since it is impossible to learn exactly the amount of gas occluded by Hampe's cupric oxide, the correction of his results will not be attempted. The residue left after the ignition of cupric sulphate can hardly contain any nitrogen; and this supposition more than accounts for the difference between the results of Baubigny's analysis and the present syntheses of cupric sulphate (see page 275).

Upon referring to the other work upon the atomic weight of copper, it is apparent that nearly all of the discrepancies have been explained. A portion of Millon and Comaille's work consisted of weighing the water formed by the reduction of cupric oxide; the reason of the low result of this part of their work is not even now evident, but at the present day a discussion of the possible causes of its error would be unprofitable. Shaw's recent result, which formerly ranked among the highest of the observed values, now appears among the lowest.

Evidently the occlusion of nitrogen by cupric oxide must have a very serious effect upon experiments in which oxygen is determined by the loss of weight of material prepared by the ignition of the basic nitrate; notably in the determination of the atomic weight of the element after the method of Dumas. When the oxide is obtained by the ignition of the metal in oxygen, the correction is of course inapplicable. Unfortunately, most of the experimenters upon the subject have omitted to state the source of their cupric oxide. The preparation used in the later experiments of Erdmann and Marchand * must have contained nitrogen; and it will be remembered that the second series of his results gave a much higher result than the first.

In view of the correction, it is remarkable that the resultant atomic weight of oxygen in this case was not even higher than 16; for the correction is about five times as large as the amount necessary to account for the difference between 15.87 and that figure. From a difference either in the mode of preparation or in the temperature of ignition, the oxide used by Erdmann and Marchand must have contained much less nitrogen than the amount found in Experiments 103 to 105; or else some opposite error must have partially counterbalanced this one. Considering the remoteness of all the experiments, a present discussion of the results is unnecessary; but the conclusions are at least sufficient to throw a serious doubt upon the applicability of cupric oxide for a quantitative source of oxygen, as well as to support the modern low atomic weight of that element. The presence of nitrogen could not seriously influence the results of Keiser or those recently obtained here; and it is evident that the material used by Noyes could have contained no occluded gas.

The use of cupric oxide prepared from the nitrate must also introduce a serious error into organic nitrogen determinations after the method of Dumas, as Frankland and Armstrong have already pointed

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* J. für prakt. Chemie, XXVI. 461.

out. The usual "wire form" of cupric oxide is not subject to this cause of inaccuracy, however.

In the near future other oxides will be investigated at this laboratory with regard to their possible occlusion of gases.

IV. Upon Typical Copper.

It has been noticed that most of the calculations described in the present paper have been referred to electrolytic copper. Whether such copper represents the typical element or not is a most important question, but is one which unfortunately cannot be conclusively answered here.

Many authorities have discussed the subject,* and both sulphur and occluded gases have been found in metal prepared in this way. Hampe has shown that the occasional presence of sulphur is probably due to minute drops of solution imprisoned between the electrode and the deposit. When pure copper was to be prepared in the present investigation, the metal was invariably detached from the dish in order to prevent such imprisonment. In the determination of copper already in solution, the current was always made as weak as possible in order to avoid the chance of error. Besides, it will be remembered that there was a slight loss rather than a gain during electrolysis.

The occlusion of gases is at worst very slight. In order to reduce the error from this cause to a minimum, the crucible which formed the negative electrode was usually coated beforehand with copper, that the initial and the final surface might be subject to the same error. To determine the amount of volatile material absorbed by electrolytic copper, very thin strips were ignited in a stream of hydrogen, with the following results: —

				Gram.
107	0.80565	gram	lost	0.00005
108	0.67724	"	"	0.00004
109	1.24158	"	"	0.00004
110	0.80712	"	"	0.00001
111	1.00616	"	"	0.00003
	Average 1 gram lost			0.00003

This correction is too small to be applied, even supposing that the method of precipitation just mentioned did not render the application

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* Soret, Compt. Rend., CVII. 733, CVIII. 1208; Hampe, *loc. cit.;* also MacIntosh, Classen, Foote, Smith, and many others.

unnecessary. The amount of hydrogen absorbed even by copper reduced from the oxide is exceedingly small. Erdmann and Marchand found that one gram of copper absorbed three one-hundredths of a milligram of hydrogen, and Dumas's results were essentially the same.* Hampe was unable to find a trace of the gas in the copper remaining from his experiments. While this correction may have a sensible effect upon the old atomic weight of oxygen, it cannot seriously effect the atomic weight of copper.

No method for the preparation of pure copper has been suggested which is not open to possible objections. The present standard of reference has the merit of simplicity. Moreover, the results of the analysis of cupric sulphate, unless concealing some unknown error, show that electrolytic copper cannot be very different from the typical element as it exists in combination, otherwise the summation of the results would not so nearly equal one hundred per cent. Again, cupric oxide gives essentially identical results, whether analyzed by reduction or by electrolysis. It must be remembered that, while some of the copper used in the present series of researches came from Lake Superior, the greater part was prepared from "chemically pure" German cupric sulphate. Some unknown constant impurity may have vitiated all the preparations, but the present evidence seems to show that pure electrolytic copper is as definite a substance as most of the other "elementary substances" to which our atomic weights are referred.† A more elaborate comparison of copper from different sources and different modes of preparation would neverthless be one of considerable interest.

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* Ann. Chim. Phys., [3], VIII. 189, 205. See also Thudichum and Hake, Jahresber. 1876, p. 966; and Johnson, Jahresber. 1878, p. 286.

† Grünwald and Brauner have independently come to the conclusion that copper is a compound. If this is the case, the compound must be a very definite one. See Chem. Soc. Abstracts, 1890, p. 434.

V. SUMMARY OF RESULTS, 1887 TO 1891.

The Atomic Weight of Copper.

$O = 16.000$.

	Ratio.		Result.
I.	$2\ Ag : Cu$	Eleven Determinations	63.601
II.	$2\ AgBr : Cu[Br_2]$	Three "	63.609
III.	$2\ Ag : Cu[Br_2]$	Three "	63.605
IV.	$[CuSO_4 - Cu] : Cu$	Three "	63.593
V.	$Na_2CO_3 : Cu$	Seven "	63.600
VI.	$Na_2SO_4 : Cu$	Four "	63.607
VII.	$Na_2CO_3 : [CuSO_4 - SO_4]$	Two "	63.621
VIII.	$Na_2SO_4 : [CuSO_4 - SO_4]$	Three "	63.641
IX.	$BaSO_4 : Cu$	One "	63.603
X.	$BaSO_4 : [CuSO_4 - SO_4]$	One "	63.625
XI.	$[CuO - Cu]$ corrected : Cu	Five "	63.604
	General Average of the eleven Series		63.610
	" " of forty-three Determinations		63.606

Of these results five — namely, I., II., III., V., and VI. — are incomparably more trustworthy than the others. Their computation involves only very accurately determined elements, and they are least affected by a given change in the molecular weights of the standards of reference. Their experimental errors are far smaller than those of any of the others, and they involve the simplest and most direct processes, and the minimum number of necessary corrections. They are in no case computed by the objectionable method of difference. Finally, each one of the five is wholly independent of the weight of any copper compound whatsoever. These reasons constitute a sufficient ground for the separation of such results from the others.

Selected Series.

	Ratio.	Salt decomposed.	If O = 16.000, Cu =
I.	$2\ Ag : Cu$	$AgNO_3$	63.601
II.	$2\ AgBr : Cu$	$CuBr_2$	63.609
III.	$2\ Ag : Cu$	$CuBr_2$	63.605
V.	$Na_2CO_3 : Cu$	$CuSO_4$	63.600
VI.	$Na_2SO_4 : Cu$	$CuSO_4$	63.607
	Final average		63.604

If the oxygen is taken as 15.96, copper becomes 63.44. With oxygen 15.87, the value sinks to 63.09.

The mathematical discussion of these results is omitted, because it gives an exaggerated notion of the accuracy of the final average. The real probable error of this average is much more dependent upon the chemical purity of the electrolytic copper than upon the mere mechanical or experimental error with which alone the theory of least squares is competent to deal.

It is apparent that any one of the methods, thoroughly investigated, would have long ago afforded a fairly accurate knowledge of the atomic weight. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labor for a reviser in the future.

In the present investigation every reaction was assumed to involve some constant error, and every substance was assumed to contain some constant impurity, until a proof of the contrary was obtained. The research consisted, in fact, of a succession of mutual checks. The attempt was made to adopt precautions of a consistent order of refinement; and the still remaining causes of possible error have been carefully pointed out in the description. The not inconsiderable outlay of time, thought, and labor has been more than repaid by a conviction of the definiteness of the combining proportions which four years ago would have seemed to the writer impossible.

XVI.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, WORCESTER, MASS.

THE ACTION OF ACETOACETIC ETHER ON QUINONES: SYNTHESIS OF BENZOFURFURAN DERIVATIVES.

By M. Ikuta.

Presented by J. U. Nef, October 14, 1891.

When chloranil is treated with sodium acetoacetic ether, one or two of its chlorine atoms can be replaced by acetoacetic ether groups. The study of the mono- and the di-substitution products obtained has led to an interesting synthesis of a number of furfuran derivatives.

Trichlorquinoneacetoacetic Ether, $C_6Cl_3O_2(C_6H_9O_3)$.

10 grams of acetoacetic ether, dissolved in about 100 c.cm. of benzine, are converted by means of sodium in the form of fine wire into the sodium salt. To the emulsion thus obtained is slowly added 18 grams (1 molecule) of finely powdered chloranil with continual shaking. The reaction sets in immediately, and the solution becomes colored blue, dark green, and finally brown. In order to complete the reaction the mass is either warmed on a water-bath or allowed to stand for several hours. The part insoluble in benzine, which is removed by filtration and repeatedly washed with fresh benzine, is a very bulky resinous mass, not practicable to work up further; it consists of sodium chloride, the sodium salts of the mono- and the di-substituted acetoacetic ether derivative of chloranil, besides much resinous matter.*

The benzine from the clear orange-colored filtrate is then distilled

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* From this portion, by acidifying and extracting with benzine and crystallizing from alcohol, a very slight amount of greenish yellow prisms melting at 183°, soluble in alkalies with blue coloration, and also dark brown needles insoluble in alkalies and melting above 270°, were obtained, but in too small quantity to admit of further study.

off, and the last traces of it removed by prolonged heating in an open dish on a water bath. A dark orange-colored oil is left, which is a mixture of acetoacetic ether, and the mono- and the di-substituted acetoacetic ether derivatives of chloranil. On adding a small amount of absolute alcohol, and stirring, the oil gradually solidifies to a crystalline mass. Recrystallized from alcohol, large orange rhombohedra of trichlorquinoneacetoacetic ether are obtained, as well as yellow rhombic crystals of dichlorquinonediacetoacetic ether, which two substances can readily be separated mechanically from one another; the latter is also somewhat less soluble in alcohol.

The red mono-substitution product was recrystallized from alcohol until it showed the constant melting point 94°, and then dried at 70° to 75° and analyzed.

0.3014 gram substance gave 0.4737 gram CO_2 and 0.0738 gram H_2O.
0.2524 " " " 0.3158 " AgCl (Carius).

	Theory for $C_{12}H_9Cl_3O_5$.	Found.
C	42.42	42.86
H	2.69	2.72
Cl	31.37	30.95

Trichlorquinoneacetoacetic ether is easily soluble in benzine, warm alcohol, and chloroform, moderately so in acetic acid, and difficultly soluble in ether. It dissolves in dilute alkalies and ammonia with blue color, changing quickly to orange-yellow on standing. An alcoholic solution of the substance gives a blood-red coloration with ferric chloride. With aniline it forms a colorless addition product melting at 146°, whereas fuming nitric acid changes it into a yellow very unstable substance. Reducing agents readily convert it into the corresponding hydroquinone.

Trichlorhydroquinoneacetoacetic Ether, $C_6Cl_3(OH)_2(C_6H_9O_3)$.

The reduction of the quinone can be effected quantitatively by dissolving it in about 6 parts of alcohol, and adding alternately zinc dust and dilute sulphuric acid in small quantity until the solution becomes colorless. On adding water the hydroquinone separates out as an oil, which soon solidifies. Recrystallized from benzine, it is obtained in colorless rhombohedra, melting at 132°.

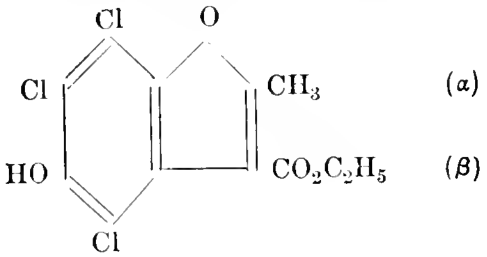
0.2204 gram substance dried at 105° gave 0.3444 gram CO_2 and 0.0707 gram H_2O.

	Theory for $C_{12}H_{11}Cl_3O_5$	Found.
C	42.20	42.61
H	3.22	3.62

The hydroquinone is difficultly soluble in most organic solvents in the cold. It dissolves in alkalies with pale yellow color, changing quickly to dark green and yellow. An alcoholic solution gives with ferric chloride a blood-red coloration (*vide* the quinone).

The most noteworthy property of this substance is the ease with which it loses water going over into a benzofurfuran derivative.

Trichlor p-oxybenzofurfuran α-methyl β-carboxylic Ether,



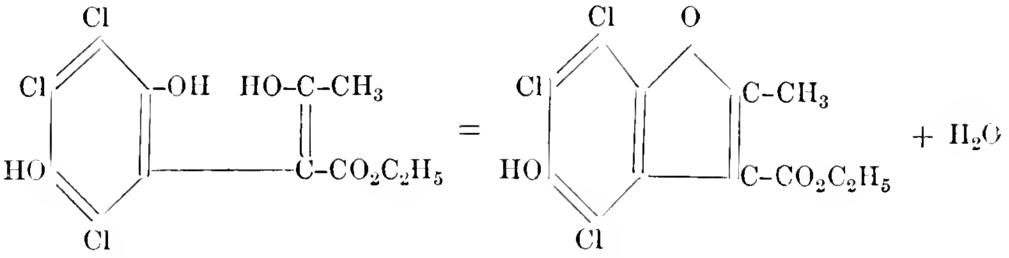
One part of trichlorhydroquinoneacetoacetic ether is dissolved in 10 parts of acetic acid, and, after adding a few drops of concentrated sulphuric acid, the solution is boiled for about an hour, or until on adding water to a portion a white precipitate is obtained which is not affected by ferric chloride. On adding a small amount of water to the hot acetic acid solution, the furfuran derivative crystallizes out in colorless transparent needles melting at 138°. The substance was recrystallized once from acetic acid, dried at 110°, and analyzed.

0.2530 gram substance gave 0.4131 gram CO_2 and 0.0672 gram H_2O.
0.2005 " " " 0.2638 " AgCl (Carius).

	Theory for $C_{12}H_9Cl_3O_4$.	Found.
C	44.51	44.53
H	2.71	2.95
Cl	32.92	32.54

The substance is easily soluble in chloroform, less so in alcohol, ether, and cold acetic acid; it gives no coloration in alcoholic solution with ferric chloride, and dissolves in alkalies forming a colorless solution. On warming with concentrated sulphuric acid, a dark reddish blue coloration is obtained, which is very characteristic of the substance, as well as of all benzofurfuran derivatives. On heating with alcoholic potash, it is saponified to the corresponding monobasic acid.

The furfuran derivative is unquestionably formed according to the following equation: —



Trichlorhydroquinoneacetoacetic Ether. Benzofurfuran Derivative.

That acetoacetic ether is not a ketone, but a phenol-like body (β-oxycrotonic ether), has been made highly probable by the work of Nef, soon to appear in Liebig's Annalen. In order, therefore, to explain the above reaction, the assumption of a pseudo or mobile modification of trichlorhydroquinoneacetoacetic ether is unnecessary; and the ease with which this anhydride formation takes place depends entirely on the position of the atoms in space.*

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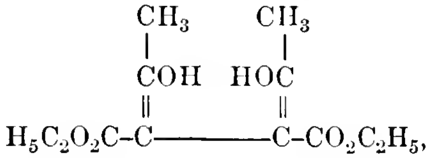
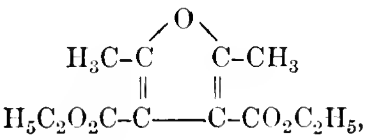
* In some cases *only* the anhydride can be obtained (see Ann. Chem. Liebig). In this connection I would like to point out, that diacetylsuccinic ether,



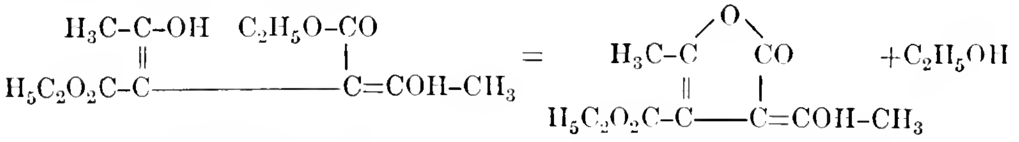
$$\begin{array}{rcl} & CH_3 & CH_3 \\ & | & | \\ & COH & HOC \\ & \| & \| \\ H_5C_2O_2C- & C\text{———} & C-CO_2C_2H_5, \end{array}$$

according to Knorr, splits off on heating either water (200°), forming the furfuran derivative,



$$\begin{array}{rcl} & \overset{O}{\diagup\;\;\diagdown} & \\ H_3C-C & & C-CH_3 \\ \| & & \| \\ H_5C_2O_2C-C & \text{——} & C-CO_2C_2H_5, \end{array}$$

(Ber. d. chem. Ges., XVII. 2863), or alcohol (170°), forming isocarbopyrotritaric ether (Ber. d. chem. Ges., XXII. 159). Knorr thinks it probable that the latter substance is a ketopentamethylene derivative, just as Fittig (Ber. d. chem. Ges., XVIII. 3410) regards pyrotritaric ether as a ketopentamethylene derivative. It is however far more probable that the splitting off of alcohol from diacetylsuccinic ether takes place as follows:

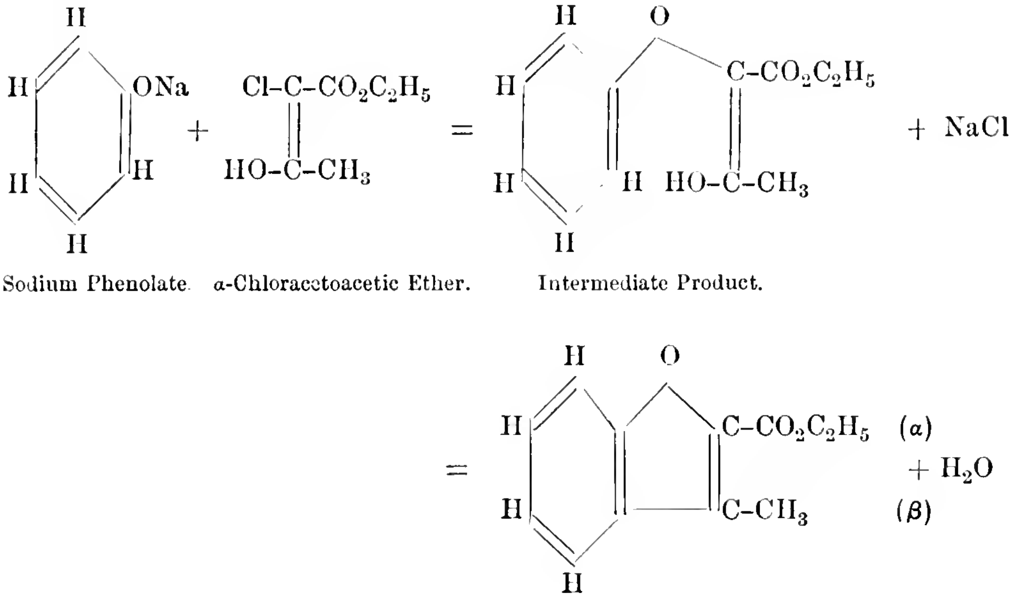


$$\begin{array}{l} H_3C-C-OH \quad C_2H_5O-CO \\ \qquad\;\; \| \qquad\qquad\qquad\;\; | \\ H_5C_2O_2C-C\text{————}C{=}COH-CH_3 \end{array} = \begin{array}{l} \qquad\quad\;\; \overset{O}{\diagup\;\;\diagdown} \\ \quad H_3C-C \qquad CO \\ \qquad\quad\;\; \| \qquad\;\; | \\ H_5C_2O_2C-C\text{——}C{=}COH-CH_3 \end{array} + C_2H_5OH$$

Diacetylsuccinic Ether. Isocarbopyrotritaric Ether

Benzofurfuran derivatives were first obtained by Fittig and Ebert* from cumarine derivatives, and later Rössing† obtained cumarone from *o*-aldehydophenoxyacetic acid.

A general method for obtaining such compounds has been published by Hantsch,‡ which consists in heating sodium salts of phenoles with *α*-chloracetoacetic ether, e. g.:



Sodium Phenolate. α-Chloracetoacetic Ether. Intermediate Product.

Benzofurfuran Derivative.

While the above method leads to *α*-methyl *β*-carboxylic derivatives, that of Hantsch leads to *β*-methyl *α*-carboxylic derivatives of benzofurfuran.

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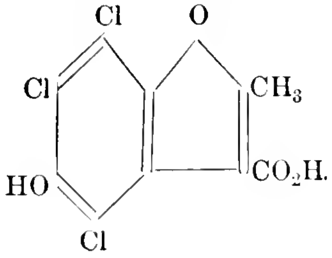
i. e. that under certain conditions of temperature the OH group of an acetyl radical is *nearer* in space to the OC_2H_5 group of a $COOC_2H_5$ group, whereas at a higher temperature (200°) the two OH groups of the acetyl radicals are *nearer* to one another in space, so that either alcohol or water is split off according to the temperature. Knorr also puts forward the above formula for isocarbopyrotritaric ether, but favors the ketopentamethylene formula because of the behavior of the ether towards alkalies (Ber. d. chem. Ges., XXII. 167). On the other hand, all the other reactions of isocarbopyrotritaric ether are best explained by the above lactone formula. It is therefore highly probable that a similar relationship exists in the very puzzling pyrotritaric acid series as has been shown by Feist (Liebig, Ann. Chem., CCLVII. 253) to exist in the case of dehydracetic acid. — J. U. Nef.

* Ann. Chem. (Liebig), CCXVI. 170.

† Ber. d. chem. Ges., XVII. 3000.

‡ Ber. d. chem. Ges., XIX. 1292, 2930, XX. 1332.

Trichlor p-oxybenzofurfuran α-methyl β-carboxylic Acid,



The ethyl ether just described is readily saponified by heating with twice the calculated amount of alcoholic potash on a water bath. After driving off the alcohol, and taking up with water, addition of dilute acetic acid precipitates the free acid in the form of colorless needles. It is purified by crystallization from glacial acetic acid, from which solvent it separates out into colorless transparent needles melting at 258° and subliming without change. The crystals become opaque on drying above 100°.

0.2736 gram substance dried at 130° gave 0.4090 gram CO_2 and 0.0439 gram H_2O.

0.2130 gram substance dried at 130° gave 0.3076 gram AgCl (Carius).

	Theory for $C_{10}H_5Cl_3O_4$.	Found.
C	40.61	40.76
H	1.70	1.78
Cl	36.04	35.72

In its behavior towards organic solvents, concentrated sulphuric acid, and alkalies, the free acid is like that of the ethyl ether.

p-Dichlorquinonediacetoacetic Ether, $C_6Cl_2O_2(C_6H_9O_3)_2$.

The method of preparing this substance is exactly the same as that described above for the mono-substitution product, except that twice as much sodium acetoacetic ether is taken. The crude product obtained is purified by crystallization from alcohol until the melting point of the substance reaches 127–128°. The alcoholic mother liquors always contain some mono-substitution product as well as greenish yellow prisms melting at 183° (mentioned in the foot-note, page 295). The substance is thus obtained in pure yellow rhombohedra or rhombic plates.

0.2492 gram substance dried at 110° gave 0.4515 gram CO_2 and 0.0944 gram H_2O.

0.3003 gram substance dried at 110° gave 0.1947 gram AgCl (Carius).

	Theory for $C_{18}H_{18}O_8Cl_2$.	Found.
C	49.88	49.41
H	4.16	4.21
Cl	16.39	16.04

The compound is easily soluble in benzine and chloroform, less so in alcohol, acetic acid, and ether. It dissolves in dilute alkalies, mild or caustic, forming deep bluish violet solutions, which soon change to brown. Sodic nitrite reacts on an alcoholic solution in the cold, forming a yellow substance which crystallizes in prisms, melts at 184°, and contains both chlorine and nitrogen. Fuming nitric acid converts the quinone into a very unstable yellow substance. An alcoholic solution is colored deep blood-red by addition of ferric chloride. One of the noteworthy properties is the ease with which the quinone forms addition products, and these are treated specially further on. A great many experiments were made in order to prove that the two acetoacetic ether groups are in the para position, but without success. This is, however, extremely probable, since in all cases yet known where two chlorine atoms in chloranil have been replaced the substitution takes place in para position (compare also Stieglitz, where two malonic ether groups are introduced in the para position *).

p-Dichlorhydroquinonediacetoacetic Ether, $C_6Cl_2(OH)_2(C_6H_9O_3)_2$.

The above quinone is reduced to the hydroquinone in exactly the same way as described under trichlorhydroquinoneacetoacetic ether. The solid obtained by adding water to the alcoholic solution is purified by crystallization from benzine, from which solvent it separates out in colorless transparent rhombohedra, melting at 154°.

0.2114 gram substance dried at 130° gave 0.3816 gram CO_2 and 0.0881 gram H_2O.

	Theory for $C_{18}H_{20}Cl_2O_8$.	Found.
C	49.65	49.23
H	4.59	4.62

In its behavior towards ferric chloride, alkalies, and solvents, the hydroquinone is quite similar to trichlorhydroquinoneacetoacetic ether. The substance treated with dehydrating agents loses two molecules of water with ease, going over into a benzodifurfuran derivative.

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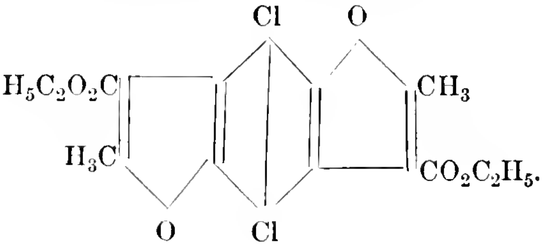
* American Chem. Journal, XIII. 38.

p-Dichlorbenzo-p-difurfuran α-dimethyl β-dicarboxylic Ether,



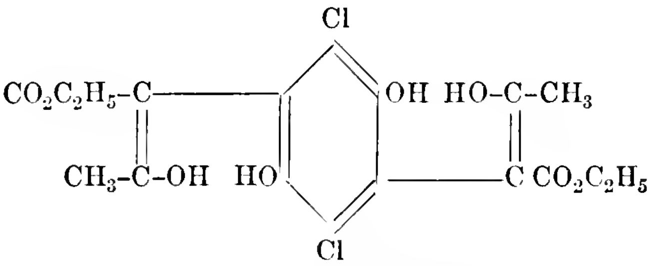
The above hydroquinone, when boiled for about an hour in acetic acid solution containing a few drops of concentrated sulphuric acid, is converted quantitatively into a benzodifurfuran derivative, which, since it is insoluble in alkalies, can easily be separated from the original substance. After precipitating by addition of water and treating with dilute sodic hydrate, the substance is crystallized from acetic acid (95%) and obtained in long transparent prisms melting at 175°.

0.2006 gram substance dried at 120° gave 0.3965 gram CO_2 and 0.0748 gram H_2O.

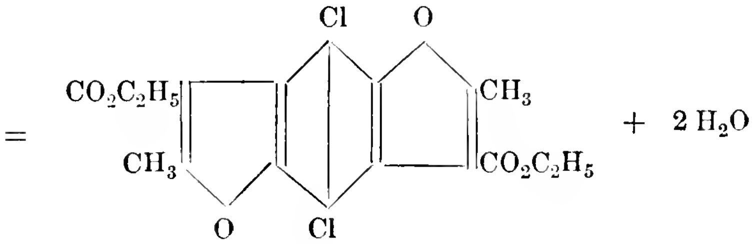
0.2647 gram substance dried at 120° gave 0.1886 gram AgCl (Carius).

	Theory for $C_{18}H_{16}Cl_2O_6$.	Found.
C	54.13	53.95
H	4.01	4.16
Cl	17.79	17.63

The furfuran compound is unquestionably formed according to the following equation : —



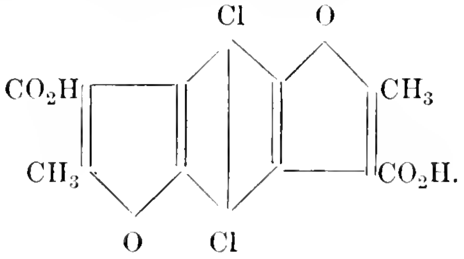
p-Dichlorhydroquinonediacetoacetic Ether.



p-Dichlorbenzo-*p*-difurfuran α-dimethyl β-dicarboxylic Ether.

The substance dissolved in concentrated sulphuric acid and warmed, gives a dark bluish green coloration which is very characteristic. It is difficultly soluble in most organic solvents except chloroform. By passing chlorine into a chloroform solution of the substance it forms a pale yellow oily addition product, which, on treating with zinc dust and acetic acid, is converted back to the original substance. Alcoholic potash saponifies it to the corresponding dibasic acid, —

p-Dichlorbenzo-p-difurfuran a-dimethyl β-dicarboxylic Acid,



The ethyl ether described above is easily saponified by heating with twice the calculated amount of alcoholic potash. After driving off the alcohol, taking up with water, and acidifying with dilute acetic acid, the free acid separates out as a fine white powder, which, examined under the microscope, consists of crystalline needles. It sublimes at a higher temperature without melting, and is insoluble in organic solvents and water. It was therefore dissolved in potassic carbonate, precipitated by dilute acetic acid, and, after thorough washing with hot water, dried at 130° and analyzed.

0.2087 gram substance gave 0.3732 gram CO_2 and 0.0482 gram H_2O.
0.2461 " " " 0.2013 " AgCl (Carius).

	Theory for $C_{14}H_8Cl_2O_6$.	Found.
C	48.95	48.76
H	2.33	2.56
Cl	20.69	20.24

Concentrated sulphuric acid gives a bluish green coloration similar to that of the ether.

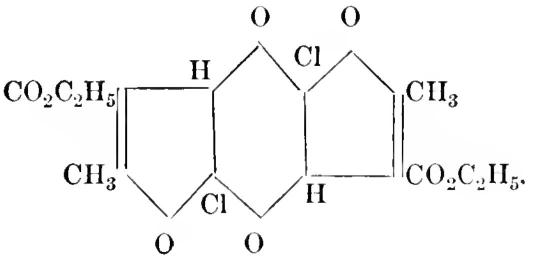
The Addition Products of p-Dichlorquinonediacetoacetic Ether.

As above mentioned, this substance is characterized by the ease with which it forms addition products. Treated in chloroform solution with one molecule of bromine, a complete absorption of bromine takes place quickly without the slightest evolution of hydrobromic acid, and a colorless odorless substance separates out in heavy scales, which melt at 216°. The analysis of the product, made at different times and washed with chloroform, gave no constant figures. The halogen determinations gave results varying from 1% to 5% too high for that calculated for a dibromide, $C_{18}H_{18}Cl_2O_8$, Br_2, and this points to the presence of some tetrabromide. That the bromine has been added to the double bonds present in the quinone group and not to the acetoacetic ether residues follows: 1st, because the substance sublimes without decomposition; 2d, the corresponding dichlorhydroquinonediacetoacetic ether is acted upon only very slowly by bromine, and then with evolution of hydrobromic acid and formation of pungent derivatives affecting the eyes; 3d, the above addition product treated with zinc dust and acetic acid, or in alcoholic solution with zinc dust and dilute sulphuric acid, is converted chiefly into *p*-dichlorbenzo-*p*-difurfuran α-dimethyl β-dicarboxylic ether.

The study of the product formed with bromine, though incomplete, is thus sufficient to show that it is an addition product, and its study, as well as that of other addition products, will be continued.

Noteworthy is the ease with which *p*-dichlorquinonediacetoacetic ether adds water, and is then converted into a new quinonefurfuran derivative.

Quinone p-difurfuran α-dimethyl β-dicarboxylic Ether Dihydrochloride,



p-Dichlorquinonediacetoacetic ether is dissolved in 3 parts of acetic acid (95%) and warmed with a few drops of dilute sulphuric acid (1 : 5) on a water bath until the orange-colored solution becomes almost colorless. On diluting with water a pale yellow substance separates out in oily drops, which soon solidify to a white crystalline solid. The yield is almost quantitative, and after crystallizing from a mixture of chloroform and ether the substance was analyzed with the following result.

0.2010 gram substance dried in vacuum gave 0.3641 gram CO_2 and 0.0746 gram H_2O.

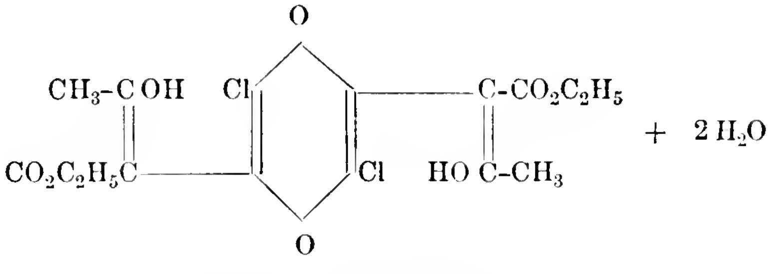
0.2112 gram substance dried in vacuum gave 0.1369 gr. AgCl (Carius).

	Theory for $C_{18}H_{18}Cl_2O_8$.	Found.
C	49.88	49.40
H	4.15	4.12
Cl	16.39	16.03

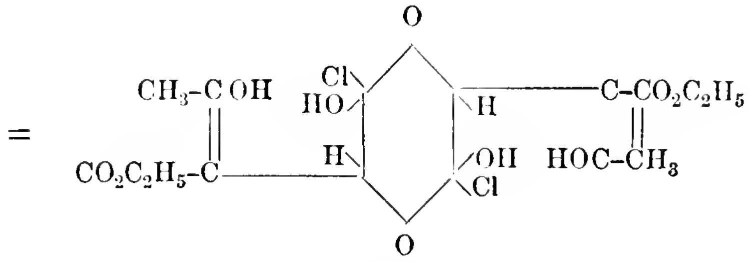
The substance melts at 171° to a pale yellow liquid, and sublimes without decomposition. It crystallizes in star-shaped leaflets or short prisms, and is easily soluble in organic solvents, but insoluble in water or mild alkalies. Warmed with concentrated sulphuric acid it gives a deep bluish green coloration, which is characteristic for furfuran derivatives.

Treated with twice the calculated amount of alcoholic potash, it is saponified to a dibasic acid, $C_{14}H_{10}Cl_2O_8$, which crystallizes from hot water in colorless needles. The acid is best purified by dissolving in soda and addition of dilute acids, when it separates out very slowly on standing. It decomposes with evolution of carbon dioxide on heating to 220°. An analysis gave results which agree closely with the formula $C_{14}H_{10}Cl_2O_8$, but show that the acid was not quite pure. (Found 43.53 % C, 2.96 % H, 20.50 % Cl. Theory, 44.56 % C, 2.65 % H, 18.95 % Cl.)

The formation of the above ester, $C_{18}H_{18}Cl_2O_8$, isomeric with *p*-dichlorquinonediacetoacetic ether is probably as follows. At first, an addition of two molecules of water takes place, just as has been observed in the case of many olefine derivatives:

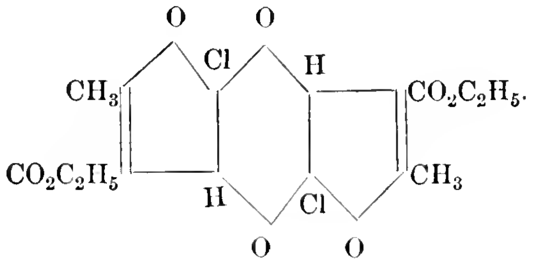


p-Dichlorquinonediacetoacetic Ether.



Addition Product.

The addition product formed then loses two molecules of water, going over into the furfuran derivative,



Benzofurfuran Derivatives from Quinone and Acetoacetic Ether.

Von Pechmann* describes a condensation product obtained from quinone and acetoacetic ether by means of alcoholic chloride of zinc. He gives it the formula $C_{16}H_{16}O_6$, and, as he states, it is formed according to the following equation:

$$C_6H_4O_2 + 2C_6H_{10}O_3 = C_{16}H_{16}O_6 + H_2O + C_2H_6O.$$

From the product $C_{16}H_{16}O_6$, he obtained further, by saponification with alcoholic potash, a dibasic acid, $C_{14}H_{12}O_6$.

Since v. Pechmann says that he does not intend to study the product obtained any further, I have taken up the investigation of these substances, especially since the behavior of the compound $C_{16}H_{16}O_6$ is very similar to the benzofurfuran derivatives obtained from chloranil, and it therefore seemed probable that it possessed a similar constitution. The formulæ given by him for the above products are deduced from the mean result of a number of analyses. It is difficult, for instance, to see how from a *neutral* substance, $C_{16}H_{16}O_6$, by saponification, a *dibasic* acid, $C_{14}H_{12}O_6$, can be formed, since the former substance is not likely to contain methoxy groups. The study of these substances soon showed that the empyrical formulæ given to the condensation product as well as the dibasic acid were incorrect.

The reaction between quinone and acetoacetic ether really takes place according to the following equation:

$$\text{I.}\quad C_6H_4O_2 + 2\,C_6H_{10}O_3 = C_{18}H_{18}O_6 + 2\,H_2O + 2\,H;$$

the two hydrogen atoms are used up in converting a molecule of quinone into hydroquinone:

$$\text{II.}\quad C_6H_4O_2 + 2\,H = C_6H_4(OH)_2.$$

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* Ber. d. chem. Ges., XXI. 3005.

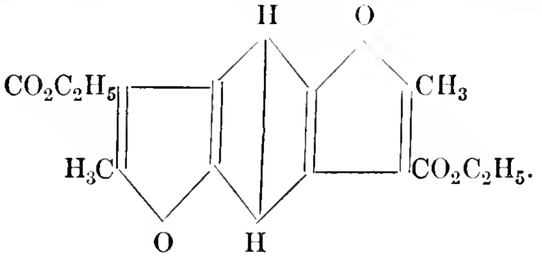
The condensation product thus has the formula $C_{18}H_{18}O_6$, instead of $C_{16}H_{16}O_6$; by saponification with alcoholic potash two molecules of alcohol are split off, as follows:

$$C_{18}H_{18}O_6 + 2\ H_2O = C_{14}H_{10}O_6 + 2\ C_2H_6O.$$

The above mentioned dibasic acid has therefore the formula $C_{14}H_{10}O_6$, instead of $C_{14}H_{12}O_6$, and indeed the previous analyses agree better with this formula.

	Theory for $C_{14}H_{10}O_6$.	For $C_{14}H_{12}O_6$.	Von Pechmann's Analysis.
C	61.25	60.80	60.80
H	3.65	4.30	3.80

Benzo-p-difurfuran α-dimethyl β-dicarboxylic Ether,



When quinone (one molecule) is heated in alcoholic solution with two molecules of acetoacetic ether in the presence of zinc chloride, the condensation product $C_{18}H_{18}O_6$ is obtained, and as regards properties, etc., I can confirm in all detail the given statements. The alcoholic mother liquors contain, however, hydroquinone as well as a new substance, $C_{12}H_{12}O_4$, described below, which products have been overlooked. The analysis of the condensation product crystallized from acetic acid, gave figures agreeing well with the formula $C_{18}H_{18}O_6$. For the combustion it was carefully mixed with powdered chromate of lead, and the results obtained prove that it contains about 2% more carbon than found by v. Pechmann. The benzofurfuran derivatives all burn with great difficulty, so that most of the analyses given in this paper were carried out with lead chromate.

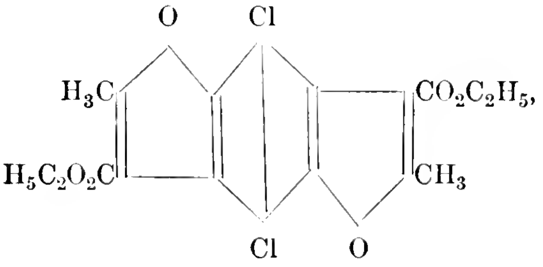
0.1942 gram substance dried at 130° gave 0.4625 gram CO_2 and 0.0983 gram H_2O.

0.2027 gram substance dried at 130° gave 0.4840 gram CO_2 and 0.1033 gram H_2O.

	Theory for $C_{18}H_{18}O_6$.	Found. I.	Found. II.	Mean of former Analyses.	Theory for $C_{16}H_{16}O_6$.
C	65.45	64.96	65.12	63.00	63.10
H	5.45	5.62	5.66	5.30	5.20

I give here, for convenience' sake, the properties of the substance.* "Colorless needles, melting at 184°. Insoluble in water or alkalies, and soluble in chloroform and boiling acetic acid. The solution in concentrated sulphuric acid turns deep blue on warming. Bromine reacts, forming a crystalline derivative. Phenylhydrazin, benzoyl chloride, and hydriodic acid have no action on the substance."

The proof that the compound $C_{18}H_{18}O_6$ has the constitution above given is as follows: chlorine converts it into a disubstitution product $C_{18}H_{16}Cl_2O_6$, which is identical with *p*-dichlorbenzo-*p*-difurfuran *a*-dimethyl *β*-dicarboxylic ether,



already described and obtained from chloranil.

The substance is dissolved in acetic acid, and chlorine is passed into the solution for several hours in the sunlight, until a portion treated with zinc dust gives on addition of water a crystalline precipitate melting from 155–160°, when the rest of the solution is treated in the same manner. By repeated crystallization from acetic acid (95%), the crude product was finally converted into a substance which melts constant at 175°, and crystallizes in long transparent needles identical in every respect with the *p*-dichlorbenzodifurfuran derivative $C_{18}H_{16}Cl_2O_6$ described above. This was also confirmed by a halogen determination.

0.2138 gram substance dried at 120° gave 0.1499 gram AgCl (Carius).

	Theory for $C_{18}H_{16}Cl_2O_6$.	Found.
Cl	17.79	17.35

The substitution of the two hydrogen atoms of $C_{18}H_{18}O_6$ is undoubtedly preceded by the formation of an addition product, just as $C_{18}H_{16}Cl_2O_6$ gives, when treated with chlorine, an oily addition product as before mentioned, but the chlorine in these addition products is easily taken out by zinc dust and acetic acid.

These results prove conclusively the constitution of the condensation product $C_{18}H_{18}O_6$; the constitution of the dibasic acid $C_{14}H_{10}O_6$

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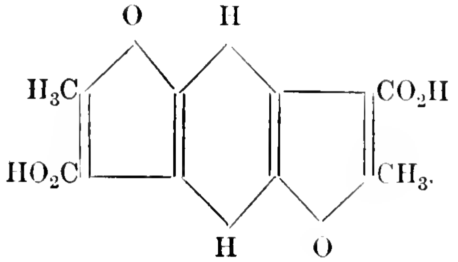
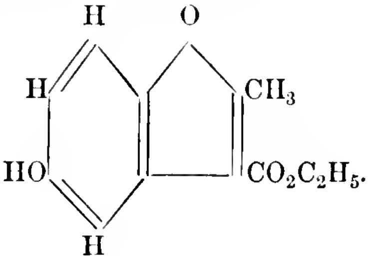
* Ber. d. chem. Ges., *loc. cit.*

obtained from it by means of alcoholic potash necessarily follows; it is a benzo-*p*-difurfuran *α*-dimethyl *β*-dicarboxylic acid,



p-Oxybenzofurfuran α-dimethyl β-carboxylic Ether,



The above alcoholic chloride of zinc mother liquors, from which the product $C_{18}H_{18}O_6$ has been removed, always contains hydroquinone and a furfuran derivative, $C_{12}H_{12}O_4$, besides acetoacetic ether. The hydroquinone was isolated, after driving off the alcohol, by taking up water and extracting the aqueous solution with ether. The condensation product $C_{12}H_{12}O_4$ is obtained by allowing the alcoholic mother liquors to evaporate spontaneously, when it separates out in pearly scales. It is formed from quinone and acetoacetic ether according to the following equation:

$$C_6H_4O_2 + C_6H_{10}O_3 = C_{12}H_{12}O_4 + H_2O.$$

The best yield (50% of quinone taken) is therefore obtained by heating quinone (1 molecule) with a molecule of acetoacetic ether in the presence of alcoholic zinc chloride. After filtering off the insoluble product $C_{18}H_{18}O_6$, which is invariably formed, the filtrate is allowed to evaporate in the air, and the pearly scales which separate out are brought on porous plates and washed with water. Recrystallized twice from petrolic ether (bpt. 70–80°), the substance is obtained in colorless scales or in flat needles, melting at 137°.

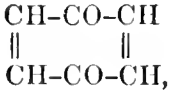
0.1889 gram substance dried at 110° gave 0.4510 gram CO_2 and 0.0997 gram H_2O.

	Theory for $C_{12}H_{12}O_4$.	Found.
C	65.45	65.12
H	5.45	5.86

The benzofurfuran derivative is insoluble in water, but, since it contains a phenol group, soluble in alkalies. It is easily soluble in most organic solvents except petrolic ether. Warmed with concentrated sulphuric acid, it gives a reddish purple color.

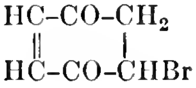
The question now arises how the formation of the condensation products $C_{18}H_{18}O_6$ and $C_{12}H_{12}O_4$ can be explained. Sarauw * has shown that, when quinone is treated with hydrobromic acid, hydroquinone and mono- and di-bromhydroquinone are found.

Since Nef † has unquestionably proved the presence of two double bonds in quinone,



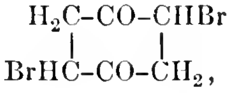
it is highly probable that the action of the hydrobromic acid is to form addition products,‡

(I.)



and

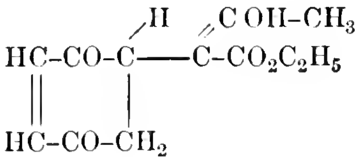
(II.)



and that these are then converted into monobrom- and *p*-dibromhydroquinone respectively, two of the hydrogen atoms in the addition product II. being removed by quinone, which goes over into hydroquinone.

It is becoming more and more apparent that all the reactions shown by quinone which have hitherto not been understood are due to the ease with which such addition takes place; the activity of the double bonds in quinone has been further shown above by the addition of bromine and of water to *p*-dichlorquinonediacetoacetic ether. It is therefore very probable that acetoacetic ether reacts on quinone, just as hydrobromic acid, forming at first addition products:

(I.)



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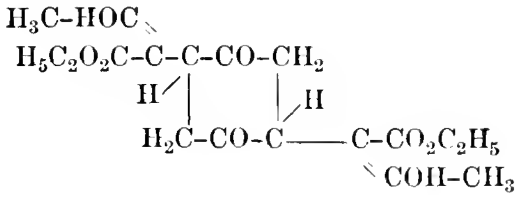
* Ann. Chem. (Liebig), CCIX. 99.

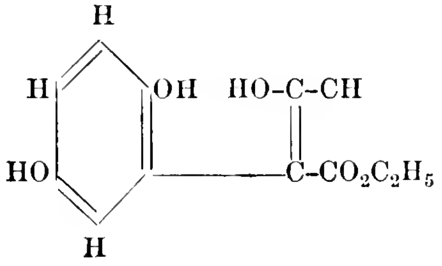
† Amer. Chem. Journal, XII. 483, XIII. 422.

‡ Amer. Chem. Journal, XIII. 427.

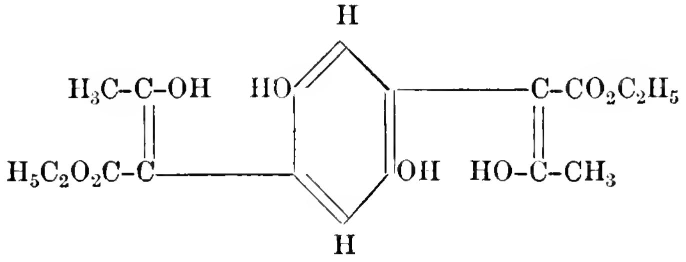
and (II.)



and that these are then converted into the hydroquinones,

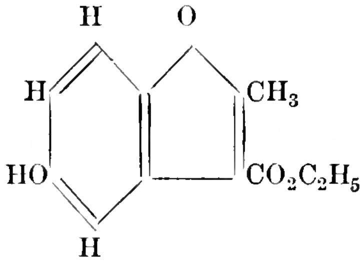


and

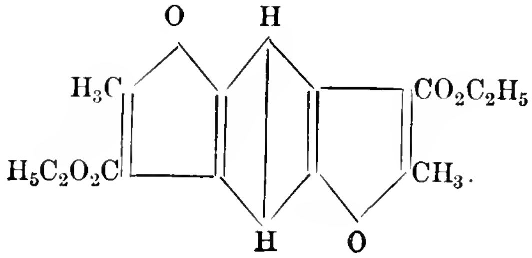


(two of the hydrogen atoms in the addition product (II.) being taken up by quinone, forming hydroquinone).

The hydroquinones just as the corresponding hydroquinones obtained above from chloranil, then lose water under the influence of the dehydrating agent present, and go over into the benzofurfuran derivatives,



and



The above explanation becomes the more probable, because the addition of acetoacetic ether in the form of the sodium salt to olefine derivatives has already been accomplished in many cases by Michael,* Auwers,† and others.

The work of which an account is given in this paper has been carried out under the direction of Prof. J. U. Nef, to whom I wish here to express my sincere thanks.

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* J. prakt. Chem. (2), XXXV. 349, 449; Michael and Freer, Ibid., XLIII. 90.

† Ber. d. chem. Ges., XXIV. 307.

Worcester, Mass., September, 1891.

XVII.

NOTE ON THE VARIATION OF MOLECULAR PRESSURE.

By Carl Barus.

Presented December 9, 1891.

1. *The Method.* — If a quantity of heat, δQ, be imparted to a substance, the result is usually expressed as $\delta U + \delta U'$, where δU is the internal, and $\delta U'$ the external work done. For liquids at atmospheric pressure, $\delta U'$ is negligible.

Regarding δU from an experimental point of view, two salient considerations present themselves. If I measure latent heats (λ), δU includes both the dissociation energy and the expansion energy necessary to effect fusion, as follows: —

a. The dissociation energy per gram necessary to change the solid molecule into the liquid molecule, isothermally, without change of volume.

b. The energy per gram for the isothermal expansion of the molecule.

c. The energy per gram for the isothermal expansion of the configuration of molecules which constitutes the given substance from solid to liquid.

If I measure specific heats isopiestically, δU includes the purely thermal energy necessary to effect changes of the body's temperature and the expansion energy, viz.: —

d. The purely kinetic energy per gram per degree, by which the solid is appreciably changed as to temperature. This is a temperature function only.

e. The energy per gram for the corresponding isothermal expansion of the molecule.

f. The energy per gram for the corresponding isothermal expansion of the configuration of molecules; with similar quantities, d', e', f', for the solid state.

The permissibility of thus separating δU into a thermal (temperature) and a volume and thermal component is given, if the isometrics are straight lines.* For liquid thymol this is very nearly true. § 10.

2. In relation to a, I shall postulate: (1) A liquid or a gas solidifies whenever, in consequence of changes of the physical or chemical environment (temperature, stress external or internal, etc.), the cohesive valency of the constituent atoms is sufficiently increased to admit of the permanent construction of a tridimensional chain, the type structure and the molecular weight of which (solid) are each a multiple of the given structure and molecular weight. (2) A gas liquefies whenever in consequence of changes of environment the cohesive valency of the constituent atoms is increased, without affording means for the permanent construction of the chain in question.

Thus, it is supposed that the same molecular nucleus is present in the three states of aggregation, and that the aggregations are produced by relatively weak affinities. Since, therefore, it is my purpose *to bring these forces to bear*, at constant external pressure, *when the molecules are at successively different distances apart*, it will facilitate reasoning to assume at the outset that the energy necessary to effect the change a, § 1, is constant as to temperature, at least within the interval 0° to 50°, under experiment. §§ 8, 9, 12.

3. In relation to b and c, § 1, conjointly, I will proceed as follows. Anywhere within the given body let a small sphere be described; and conceive the expansion work between solid and liquid done within this sphere by the applied heat to be represented by the isothermal expansion against a pressure, p, acting on the surface of the sphere. Then p may be called the molecular pressure and the expansion work will be,

$$w = \int p \, d v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

4. Now, if a substance can be found which under the same pressure may be kept either in the solid or in the liquid state through a considerable range of temperature, then if the latent heats within this range regarded as functions of temperature, be co-ordinated with the corresponding volume changes solid-liquid, relations for the energies b and c, § 1, are deducible.

Again, if with the knowledge of b and c in hand, specific heat regarded as functions of temperature, be co-ordinated with the corresponding thermal expansions, the characters of the energies e and f,

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* Fitzgerald, Proc. Roy. Soc., Vol. XLII. p. 50, 1887.

for the solid and the liquid state, respectively, are more nearly ripe for discussion.

This, in brief, is my method. What it thus far has yielded I will now indicate.

5. *Thermal Expansion.* — In virtue of the occurrence of volume lag,[*] or hysteresis, substances of the kind needed in § 4 are forthcoming. I infer, therefore, that as regards isopiestic thermal expansion the liquid and the solid, as well as the gas, obey certain ideal laws, which may be conceived to hold good even though temperature be decreased below condensation or solidifying points, indefinitely.

I have worked with the beautifully crystalline solid thymol, which melts slightly below 50° C., and when freshly distilled can be cooled even below 0° C.

TABLE I. — EXPANSION OF THYMOL, $v = \frac{v_0}{1 - k\theta}$.

Substance.	$v_0 \times 10^5$.	$k \times 10^7$.	Temperature Interval.	No. of Observations.	Remarks.
Solid	96293	$2300 + 9\theta$	0° – 32°	8	Pyknometer measurements.
"	96369	2456	0 – 34	10	Expansions of powdered thymol under water.†
"	*96306*	*$2456 + 2\theta$*	0 – 33	10	
"	96579	$2300 + 3\theta$	0 – 34	6	Expansions of a single lump under mercury ‡
"	96565	$2200 + 6\theta$	0 – 34	5	
"	96565	$2260 + 6\theta$	0 – 41	7	
"	96584	$2100 + 9\theta$	0 – 44	10	
Liquid	*101128*	*$7600 + 2\theta$*	0 – 46	12	Pyknometer measurements.
"	101128	$7500 + 6\theta$	0 – 53	5	Pyknometer measurements, liquid boiled in vacuo. Air also expelled by vacuum solidification.

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[*] Am. Journal, Vol. XLII. p. 125 *et seq*, 1891. Cf. Vol. XXXVIII. p. 408, 1889; Vol. XXXIX. pp. 490–494, 1890.

† Evaporation in the first set not allowed for; hence the high $v_0 = .96369$.

‡ The lump unavoidably contains vacuities and fissures within. Powdered thymol cannot be put under mercury, free from air.

Measurements of thermal expansion made with a variety of methods gave me the data of Table I. They have been conveniently put in the form of an equation (Mendeleeff), $v = v_0 / \overline{1 - k\theta}$, where v is the specific volume of thymol at θ° C., and k is all but constant as to temperature.

The discrepancies here observed are easily explained, being in part due to unavoidable insufficiencies of the methods, and in part to the special properties of thymol. The numbers in Italics correspond to the conditions under which the calorimetry must be done, and are therefore selected.

It will be seen that at zero the difference of specific volumes solid-liquid is about .0185 c.c., whereas at 50° the same difference has increased to .0760 c.c., an increase of more than 50%. This cannot be regarded as a mere differential. Indeed, the relations are such that the curves if prolonged intersect at about —100°, after which the volume of the solid exceeds that of the liquid. In other work * I referred to the same point as the transitional temperature, and inferred it from the tendency of the volume lag to vanish when temperature is decreased below a certain value. The new evidence in favor of a continuous passage of the normal type of fusion into the ice type is noteworthy. Solidification contraction decreases with temperature at a rate very much more rapid than the coefficients of expansion.

6. *Latent Heat.* — A general survey of my best results for latent heat (λ) are given in the following table, for the intervals of temperature specified.

TABLE II. — LATENT HEAT OF THYMOL VARYING WITH TEMPERATURE.

Temperature Interval.	λ	Temperature Interval.	λ	Temperature Interval.	λ
3°.2–5°.1	23.0	25°.9–30°.7	26.3	35°.6–37°.7	22.6
4.2–6.1	23.4	25.8–30.4	26.9	35.1–39.0	23.4
2.5–4.7	24.8	25.8–30.4	26.9	36.2–39.2	22.7
		25.7–30.3	26.9	36.0–39.6	26 0
				36.4–39.9	23.7
Mean. 4°.9	Mean. 23.7	Mean. 28°.1	Mean. 26.8	Mean. 37°.5	Mean. 23.7

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* Am. Journal, Vol. XLII. p. 145, 1891.

The difficulty in obtaining such results is excessive; for, apart from the serious complications of the method itself, (thus it takes hours before complete solidification sets in at the higher temperatures, and minute stages must be observed in order to allow for radiation,) the observer is dealing with an (under-cooled) substance, which at the mere suggestion of careless handling begins to freeze prematurely, and which in the liquid state tends to become impure by absorption of air or water vapor. These decompositions are gradual, yet they cannot be disregarded, because they lower the melting point and thus induce early partial fusions and late complete solidifications. The table also shows the difficulty in working at other than room temperature.

7. *Specific Heat.* — For the reasons just stated, I shall have to give my data for the specific heat of thymol provisionally; for though I made such experiments with great care and in considerable number, I was not at the time fully conversant with the variety of precautions to be taken to keep the substance pure.

TABLE III. — Specific Heat of Solid and of Liquid Thymol.

Substance.	Temperature Interval.	Specific Heat.	Substance.	Temperature Interval.	Specific Heat.
Solid	20°–32°	.388	Liquid	25°–54°	.508
"	22–43	.430			
Solid	22–32	.374	Liquid	22–38	.506
"	22–43	.429	"	23–51	.515
"	22–48	.643			
"	24–49	.969			
Solid after distillation	26–41	.504	Liquid distilled	26–42	.509

These data, obtained with different charges, are much below the sensitiveness of the method. The values for solid thymol, moreover, show the unreasonably large influence of temperature, accounted for in § 6.

8. *Molecular Pressure.* — Taking the data of Table II. at their face value, the only justifiable conclusion to be derived is that λ is constant for the interval 0° to 40°. Within the same interval the differ-

ences of specific volume increase from .048 c.c. to .071 c.c., nearly 50%. Hence, if either of these quantities be more than a vanishing increment, their difference must also be.

From a different point of view: if the dissociation energy, q, is large as compared with the expansion energy, then the thermal constancy of λ is of little consequence here. I make the supposition, therefore, that q is not large relative to $\int p\, d\,v$, a point which I will endeavor to test in § 12.

Returning to equation (1), § 3, it therefore follows experimentally that

$$q_0 + \int_{v_0}^{V_0} p\, d\,v = q + \int_{v}^{V} p\, d\,v \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where q_0 and q are the dissociation energies, p the molecular pressure, v_0 and V_0 the specific volumes solid and liquid respectively at zero Centigrade, and where v and V have the same meaning at any given temperature between zero and the melting point. If by § 2, $q_0 = q$, then equation (2) may be reduced to

$$\int_{V_0}^{V} p\, d\,v - \int_{v_0}^{v} p\, d\,v = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

an equation in which the molecular pressure is expressed in terms of the thermal expansion of the liquid and the solid within the same thermal limits, and by which any reasonable law of internal pressure may be preliminarily tested.

Now suppose these integrations be successively taken at zero, and all succeeding stages up to the melting point: then will the distance apart of the limits of either term vary in any ratio relative to the distance apart of the limits of the other. An equation

$$p\,(V - \varkappa) = c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

will therefore at least partially satisfy (3). In how far it may do so throughout the whole interval 0° to 50° may be gauged by determining the constancy of $\varkappa$ throughout this interval. This is done in the next table, where v, V, and $\varkappa$ are given for successive temperatures θ.

The constancy of $\varkappa$ is thus marked, and quite within the range of experimental errors; and hence the equation (4) expresses the law of force as well as any other function fitted to equation (3).

TABLE IV. — VALUES OF κ.

θ	v	V	κ	Mean κ
0°	.96300	1.01128	.94140	.94145
30	.97035	1.03508		
10	.96540	1.01905	.94148	
40	.97289	1.04334		
20	.96785	1.02698	.94148	
50	.97550	1.05178		

Since $\varkappa$ is the minimum volume to which the liquid may be reduced when pressure increases indefinitely, it is interesting to note that this volume is $(1.05 - .94)/1.05$, or 10% below the liquid volume at the melting point. Amagat * found that even at 3,000 atm. the volume of water at 17°.6 was not decreased more than 10%. Again, $\varkappa = .9415$ is very near the volume of solid and liquid thymol at the transitional temperature, this volume being .9420. Thus throughout this tentative work a certain degree of consistency is apparent, always remembering that the approximations $q_0 = q$ and $p_0 = p$ is not vouched for.

9. Equation (4) may be regarded as a point of departure from which the further construction of the equation may be attempted. Thus it is next in place to endeavor to ascertain how temperature may be said to lurk in the quasi constant, $p\ (V - \varkappa)$. In a substance like thymol, which boils at 233°, the interval 4°–40° is too small to bring out thermal variations appreciable by the above method. Hence the deduction from (2), if $p\ (V - \varkappa) = \varphi\ (T)$, though easily integrable, is not as yet available. I have therefore sought to throw some light on the thermal variations of p, and on the relative importance of $q - q_0$ by other methods.

In the first place I will note the possibility of getting rid of considerations relative to the thermal variation of the dissociation energy, q, as follows.

Suppose the specific heat at constant volume is the same for the

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* Amagat, Compt. Rend., Tom. CIII. p. 429, 1886. According to Rücker (Nature, Vol. XLI. p. 362, 1890) converging lines of evidence show that liquids cannot be compressed more than .2 or .3 of their normal bulk.

liquid and for the solid, kept at the same volume and temperature. Suppose also that the solid and the liquid isopiestics for a given pressure do actually intersect at the transitional temperature, § 5. If, therefore, the latter be taken as a point of departure, the total energy communicated to the liquid up to the temperature t and volume V, when a is the transitional volume, will be

$$q + \int_a^V P\,dV + F(t),$$

where the three terms represent dissociation, expansion, and purely thermal energy, respectively. The corresponding total energy imparted to the solid up to the temperature t will be

$$0 + \int_a^v p\,dv + f(t),$$

a being the common volume at the transitional temperature. The difference between these quantities is the latent heat, λ, at t. Hence the increase of latent heat from t_0 to t will be, (since λ is constant, and $F(t) - f(t)$ is assumed to be constant,)

$$\int_{V_0}^{V} P\,dv + \int_{v_0}^{v} p\,dv = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3')$$

an equation which differs from equation (3) in so far as P and p denote the internal pressures for the liquid and the solid states respectively, under conditions in which external pressure is pronouncedly variable. The equation (3′) would still apply if the specific heats at constant volume differ only by a constant appreciably within the limits of observation (0°–50°), but it is not available for practical comparisons.

10. *The Isometrics.* — Some time ago I showed* that within a range of 1,000 atmospheres of external pressure, at least, and within reasonable limits for the thermal stability of organic bodies, the isometrics of liquids, and particularly of thymol,† are very nearly straight. Thus the extension of equation (4) would be

$$(p + p')\,(V - \varkappa) = c\,T,$$

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* Phil. Mag., (5,) Vol. XXX. p. 348, 1890.

† Ibid., p. 358, and Plate XI.

where p' is the external pressure and T is temperature. In my experiments, only a single value of volume is introduced, and hence the work is not further available. Referring to the intrinsic equation of Ramsay, Young, and Fitzgerald (*loc. cit.*, p. 51),

$$p' = R\,T/(v - v_0) - \mu/v^n,$$

so that here the internal pressure has the form $p = \mu/v^n$.

11. *Isothermals.* — The question ceases to retain so simple an aspect when the isothermals of liquids are considered. Of the two equations which I discussed in my work* on the compressibility of liquids, viz.:

$$\frac{dV}{dp'} = -\frac{\theta}{1 + \alpha p'} \quad \text{and} \quad \frac{dV}{dp'} = -\frac{\mu}{(1 + \nu p')^2} \quad . \quad . \quad (6)$$

where p' is the external pressure, and θ, α, μ, ν are constants, the latter is at once compatible with the results of § 9. For equation (3) leads to

$$\frac{dV}{dp} = -\frac{\phi(T)}{p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and hence in equation (4), $1/v = p$ is the internal pressure active under the isothermal circumstances of compression, and

$$\phi\,(T) = \mu/\nu^2.$$

The results actually found for thymol are given in Table V., T being the absolute temperature of the isothermals, and pressures being in atmospheres.

TABLE V. — COMPRESSIBILITY OF THYMOL, $\frac{dV}{dp} = -\frac{\mu/\nu^2}{(1/\nu + p')^2}$.

T	$\mu \times 10^6$	$\nu \times 10^6$	$1/\nu$	μ/ν^2	Remarks.
°			Atm.		
301	66	300	3370	750	Initial pressure, $p'_0 = 20$ atm.
338	73	330	3050	680	Interval of observation, 400 atm.
373	97	435	2300	510	μ/ν = const. = .222.
458	162	730	1370	304	Melting point, 49°.5 C.
583	481	2160	460	102	Boiling point, 233° C.

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* Am. Journal, (3,) Vol. XXXIX. pp. 497 and 506, 1890.

Thus it is seen that the internal pressures ($1/v$) decrease from a value of nearly 4,000 atm. at zero Centigrade, indefinitely. The same is true of μ/v^2, but in neither case are the observations sharp enough to indicate the nature of this variation. Indeed, to co-ordinate all the results, I used the smoothing process $\mu/v =$ const. Hence I shall have to sketch the mere trend of the data here involved, by grouping the values μ/v^2 along some mean straight line like $.29\ (560 - T) = \varphi\ (T)$, wherein preference is given to low temperatures. Thus the volume equation takes the form

$$(V - \varkappa) = \frac{2.9\ (560 - T)}{p + p'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

When $p = -p'$, the liquid will boil, and consequently, since $v - \varkappa$ remains finite, $T = 560$. This number stands not unreasonably for the absolute boiling point of thymol at the external pressure p', which in the last table is 20 atmospheres.

12. The question now arises how the result (8) compares with the calorimetric equation

$$q + \int_v^V p\,dv = \lambda,$$

where $\lambda = 25$ is at the outset considered constant as to temperature.

Availing myself of equation (8), expressing pressures in degrees per square centimeter instead of in atmospheres, and remembering that Joule's equivalent is 4.2×10^7, I find

$$\int_v^V p\,dv = \frac{2.9}{42} \times (560 - T) \times ln\,\frac{V - \varkappa}{v - \varkappa} \quad . \quad . \quad . \quad (9)$$

Table IV. shows that throughout the interval 0° to 50°

$$ln\ (V - \varkappa)\ /\ (v - \varkappa) = 1.18 \text{ nearly.}$$

Hence the values of the dissociation energy q are in gram calories,

0°	$p\,dv = 23.4$	$q = 1.6$
20°	21.8	3.2
40°	20.1	4.9

Thus the dissociation energy is small as compared with the expansion energy; but q increases with temperature which is unreasonable. To explain this discrepancy it is necessary to revert to Table II., supposing the constancy of λ no longer tenable. Thus it appears that the march of q is within the errors of λ, and hence it has no meaning. Cf. § 9. It follows, in general, therefore, that the results obtained in measurements of the compressibility of thymol are not inconsistent with the calorimetric data; and it has thus been brought out, inasmuch as the dissociation energy is not large relative to the expansion energy, that the premises of § 8 are sustained.

13. *Energy and Volume.* — I have finally to touch upon the data obtained for specific heat, and their bearing on the purely thermal energy of thymol. It is interesting in the first place to compare the heat absorbed per unit of volume increase in the solid state, the liquid state, and during the change of state from solid to liquid. This has been done in the following table.

TABLE VI. — VOLUME RELATIONS OF THERMAL CAPACITY.

Liquid Interval 22° to 38°.	Fusion	Solid Interval 22° to 32°.
Mean spec. heat, .506	Latent heat, 25.4	Mean spec. heat, .381
Mean volume increase .01307 c.c. Coefficient .000817	Volume increase, .0589 at 19°.3 .0655 at 31°.8	Mean volume increase . . .00250 Coefficient . .00025
Ratio $\frac{\Delta Q}{\Delta v}$ 620	430 390	1520

Thus it appears that the energy expended per unit of volume increment is in marked degree greater for the solid than for the liquid state, and is greater in both of these states than during the intermediate fusion.

14. Sufficient data are now in hand for the computation of the specific heat at constant volume of thymol. Applying the well known thermodynamic relations (cf. Clausius, Chap. VIII., § 5) at 29°, Table V. shows $(d\,V_\theta/d\,p) = 66/10^{12}$ in terms of dynes per square centimeter and atmospheric pressure nearly. Under the same conditions $(d\,V_p/d\,\theta) = 801/10^6$ from Table I. Hence the specific heat at constant volume C_v is, from Table III.,

$$C_v = .506 - \big((29 + 273)/42 \times 10^6\big)\big((801)^2/66\big) = .436,$$

or about .86 of the specific heat at constant pressure $C_p = 506$.

The value $C_v = .44$ is larger than the solid specific heats at constant pressure for the same interval (Table III.), and hence *a fortiori* larger than the corresponding solid specific heats at constant volume, which are as yet indeterminable. § 9.

With this result, a direct computation based on equation (9) above may be compared. Integrating between 22° and 38° (Table VI.), — i. e. between the specific volumes 1.02860 and 1.04167, — the expansion energy is found to be 2.56 to 2.42 g. cal., according as the molecular force at the beginning or the end of the interval is inserted. The total energy imparted within this interval is $.506 \times 16$. Hence the purely thermal energy per degree between 22° and 38° has the mean value of .35, or about two thirds the specific heat at constant pressure.

Compared with the preceding datum, .44, this result is considerably too small; i. e. the expansion energy applied is about twice as large as its true value. I might point this out as an indication of the difficulty encountered in deducing internal pressure from the curvature of the isothermals (§ 11); but the true nature of the discrepancy is an error in principle, since the change of internal pressure with temperature must be radically different when the body is kept at constant external pressure in one case, and at constant volume in the other. Hence I do not regard the present result as conflicting with § 12.

15. *Melting Point and Pressure.* — The data of Tables I. and II. suffice for a preliminary computation of this value. Using the notation of Clausius (Wärmetheorie, Chap. VII., § 2), Table I. shows that at $T = 50°$ (melting point, nearly), $\sigma - \tau = .0763$. From Table II. the mean value (0°–50°) of r' is 24.7, the minimum value 23, and the maximum 27. Hence, if pressures be expressed in atmospheres instead of dynes per sq. cm., the mean relation of melting point to pressure is $d\,T/d\,p = .024$; or, more clearly,

$$.025 > d\,T/d\,p > .022,$$

where the upper limit is probably more nearly correct. This value lies well within the margin of data (.020 to .036) thus far in hand, and found with wax, paraffine, spermaceti, and naphthalene. From a perusal of my work on the continuity of solid and liquid,* it appears clearly, however, that a more accurate value of $d\,T/d\,p$ is obtainable from direct experiment, from which a value for latent heat may then be computed by inverting the thermodynamic equation.

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* Am. Journal, Vol. XLII. p. 144, 1891.

16. In the above paragraphs I have endeavored to exhibit the stage of progress attained in the work on molecular pressure, at the time when it had to be abandoned; for the calorimetric work can only be satisfactorily done in midwinter. Cf. §§ 5, 6, 7. It will be seen, I think, that the subject, as a whole, is ripe for sharper tests, and the work will therefore be resumed at an early opportunity.

Physical Laboratory, U. S. G. S.,
Washington, D. C.

PROCEEDINGS.

Eight hundred and thirty-third Meeting.

May 27, 1890. — ANNUAL MEETING.

The VICE-PRESIDENT in the chair.

The Corresponding Secretary read an obituary notice of the late Rowland G. Hazard.

The following gentlemen were elected members of the Academy: —

Henry Newell Martin, of Baltimore, to be an Associate Fellow in Class II., Section 3, in place of the late John C. Dalton.

Sir Henry Enfield Roscoe, of London, to be a Foreign Honorary Member in Class II., Section 1, in place of the late James P. Joule.

On the motion of the Corresponding Secretary it was

Voted, To meet, on adjournment, on the second Wednesday in June, at half-past seven o'clock.

The Treasurer's report was read and accepted.

The report of the Librarian was read and accepted.

On motion of the Corresponding Secretary it was

Voted, To appoint a committee to consider a proposed change in the statutes as they affect annual assessments.

The Treasurer, the Recording Secretary, and Dr. H. W. Williams were appointed.

Voted, To appropriate the sum of twenty-five hundred dollars ($2500) for the expenses of publication for the ensuing year.

Voted, That an appropriation of twelve hundred dollars ($1200) be made for the purchase and binding of books for the ensuing year.

The annual election resulted in the choice of the following officers: —

Joseph Lovering, *President.*
Andrew P. Peabody, *Vice-President.*
Josiah P. Cooke, *Corresponding Secretary.*
William Watson, *Recording Secretary.*
Eliot C. Clarke, *Treasurer.*
Henry W. Haynes, *Librarian.*

Council.

Amos E. Dolbear,
Arthur Searle,
William E. Story,
of Class I.

William G. Farlow,
Samuel H. Scudder,
David W. Cheever,
of Class II.

William Everett,
Martin Brimmer,
Edward J. Lowell,
of Class III.

Rumford Committee.

Wolcott Gibbs,
John Trowbridge,
Josiah P. Cooke,
Joseph Lovering,
George B Clark,
Erasmus D. Leavitt,
Benjamin O. Peirce.

Member of the Committee of Finance.

Thomas T. Bouvé.

The following papers were presented by title: —

On Electrical Oscillations or Waves. By John Trowbridge and W. C. Sabine.

On the Spectroscopic Study of Electrical Waves. By John Trowbridge.

On the Action of Nitric Acid upon Bromtrinitrophenylmalonic Ester. By C. Loring Jackson and W. B. Bentley.

On the Action of Sodic Alcoholates on Nitrotribrombenzols. By C. Loring Jackson and W. H. Warren.

Eight hundred and thirty-fourth Meeting.

June 11, 1890. — ADJOURNED ANNUAL MEETING.

The PRESIDENT in the chair.

The report of the Council was read and accepted.

The following report was read: —

The Rumford Committee present the following brief report for the year ending with the annual meeting of 1890.

1. The Committee have had under consideration several applications for grants from the income of the Rumford Fund, to assist in meeting the expense of original investigations relating to light or heat. They have acted favorably upon only one of these applications, and their report upon it was approved by the Academy on October 5, 1889.

2. The Committee have also given much time to the discussion of the relative claims of various suitable candidates for the Rumford Medal; but they are not yet prepared to make any recommendation upon that subject.

Respectfully submitted,

JOSEPH LOVERING, *Chairman.*

June 11, 1890.

The report of the committee appointed to consider a proposed change in the statutes as they affect annual asssessments was read and accepted.

On the motion of the Corresponding Secretary it was

Voted, That a committee, consisting of the Recording Secretary and Messrs. H. W. Williams and H. G. Denny, be appointed for the better ordering of the meetings of the Academy.

Remarks upon the subject were made by Judge Nathaniel Holmes, Dr. Williams, and the Recording Secretary.

The President appointed the following standing committees: —

Committee of Publication.

JOSIAH P. COOKE, WILLIAM G. FARLOW,
JOHN C. ROPES.

Committee on the Library.

HENRY P. BOWDITCH, AMOS E. DOLBEAR,
EDWARD J. LOWELL.

Auditing Committee.

HENRY G. DENNY, THOMAS T. BOUVÉ.

The following papers were presented by title: —

On the Candle Power of Incandescent Lamps, as related to Current, Voltage, and Energy consumed. By Louis A. Ferguson and David A. Center.

Notes on Zonaria variegata. By Herbert M. Richards.

The Recording Secretary called the attention of the Academy to the proposed monument to be erected at Gennevilliers, near Paris, to the memory of the celebrated sanitarian, Alfred Durand-Claye.

Professor Dolbear made a communication on Vortex Rings, and remarks on this subject were made by Professor Story.

Eight hundred and thirty-fifth Meeting.

October 8, 1890. — STATED MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a letter from the President of the Academy of Natural Sciences at Catania, announcing the death of Orazio Silvestri, Professor in the University of Catania; also, a letter from the President of the Geographical Society of Berne, announcing the approaching meeting of the International Geographical Congress of 1891.

Sir William Bowman, Bart., of London, was elected a Foreign Honorary Member in Class II., Section 4, in place of the late Franz Cornelis Donders.

On the motion of the Treasurer it was

Voted, That Section 2 of Chapter I. of the statutes be amended by substituting for it the following: —

"2. Fellows, resident in the State of Massachusetts, only, may vote at the meetings of the Academy. Each Resident Fellow shall pay an admission fee of ten dollars and such annual assessment, not exceeding ten dollars as shall be voted by the Academy at each annual meeting."

Voted, That the assessment for the current year be five dollars.

The following papers were presented by title: —

On the Composition of Certain Petroleum Oils and Refining Residues. By Charles F. Mabery.

The Analysis of Cupric Bromide, and the Atomic Weight of Copper. By Theodore W. Richards.

The Effect of Electrical Oscillations on the Molecules of Iron. By John Trowbridge.

A biographical notice of James Prescott Joule was read by Professor Dolbear.

Eight hundred and thirty-sixth Meeting.

November 12, 1890. — MONTHLY MEETING.

The PRESIDENT in the chair.

Mr. George B. Clark made a communication on telescope lenses.

The following papers were presented by title: —

On the Influence of the Strength of the Magnet in a Magneto Telephone Receiver. By Charles R. Cross and Harry E. Hayes.

On Electrical Condensers. By Charles Nutt.

Eight hundred and thirty-seventh Meeting.

December 18, 1890. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a letter from the International Congress of Ornithology, inviting the Academy to send delegates to its approaching meeting at Budapest in May, 1891; also, a letter from the American Chemical Society, giving notice of its next meeting, and inviting all chemists to be present.

A paper by Dr. Oliver W. Huntington, entitled "A New Meteoric Iron from Stutsman County, South Dakota," was presented by title.

A notice of the late Maria Mitchell, written by her brother, Henry Mitchell, was read by the Corresponding Secretary.

Eight hundred and thirty-eighth Meeting.

January 14, 1891. — STATED MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a communication from the Massachusetts Historical Society, inviting the Academy to send two delegates to its Centennial Anniversary on January 24, 1891; and it was

Voted, To accept this invitation, and to appoint the President and one Fellow of the Academy, to be selected by him, as delegates.

The following gentlemen were elected members of the Academy: —

Arthur Messinger Comey, of Somerville, to be a Resident Fellow in Class I., Section 3.

Charles Edward Munroe, of Cambridge, to be a Resident Fellow in Class I., Section 3.

John Ulric Nef, of Worcester, to be a Resident Fellow in Class I., Section 3.

Theodore William Richards, of Cambridge, to be a Resident Fellow in Class I., Section 3.

Charles Robert Sanger, of Cambridge, to be a Resident Fellow in Class I., Section 3.

The President, as chairman of the Rumford Committee, reported the recommendation of the Committee, that one hundred dollars be appropriated from the income of the Rumford Fund to assist Dr. E. H. Hall in his study of the periodic changes in the walls of a steam-boiler.

Also, that two hundred dollars be appropriated from the same income to assist Professor B. O. Peirce in his investigation on the conduction of heat in the interior of solid bodies. It was accordingly

Voted, That the Treasurer be authorized to pay these appropriations from the income of the Rumford Fund.

Voted, That the sum of two hundred dollars be appropriated to defray the expenses of the social meetings of the Academy for the present year.

Professor Amos E. Dolbear read a paper on Electro-magnetic Waves.

Professor W. G. Farlow presented, by title, a paper by Roland Thaxter, entitled, "Supplementary Notes on North American Laboulbeniaceæ."

Eight hundred and thirty-ninth Meeting.

February 11, 1891. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read the following letters: from the National Society of Horticulture of France, inviting the Academy to send delegates to the Seventh Horticultural Congress, to be held at Paris in 1891; from the Secretary of the Society of Natural Sciences at Milan, announcing the death of Professor Antonio Stoppani; from Professor Charles E. Munroe, acknowledging his election as a Fellow of the Academy; and from Mr. William C. Collar, resigning his Fellowship.

Professor Mark presented, by title, "A Preliminary Notice on Budding in Bryozoa."

Eight hundred and fortieth Meeting.

March 11, 1891. — STATED MEETING.

The PRESIDENT in the chair.

In the absence of the Recording Secretary, Professor Haynes was appointed Secretary *pro tem.*

The Corresponding Secretary announced the decease of members since the 29th of May, 1890, as follows: —

Henry Jacob Bigelow, Charles Otis Boutelle, and William Prescott Dexter, Resident Fellows; George Bancroft, John Charles Fremont, and Christian Henry Frederick Peters, Associate Fellows.

The following correspondence was presented: a letter from the President of the Royal Academy of Sciences of Belgium, announcing the death of its Permanent Secretary, Jean Baptiste Joseph Liagre; and a circular from the Committee of Organization of the Fifth International Congress of Geologists, inviting the members of the Academy to attend the meeting of the Congress in Washington in August next.

Professor Henry P. Bowditch brought to the attention of the Academy a circular, signed by numerous men of science, soliciting subscriptions for a marble bust and medal in commemoration of the seventieth birthday of Hermann von Helmholtz.

Professor Farlow presented, by title, a paper by W. Albert Setchell, entitled, "Preliminary Notes on the Species of Doassansia, Cornu."

Professor Dolbear gave an account of his researches to discover evidence of momentum from electrical action.

Dr. William Everett spoke at length upon the deficiencies of elmentary text-books in secondary schools.

Eight hundred and forty-first Meeting.

April 8, 1891. — MONTHLY MEETING.

The Academy met at the Harvard Medical School, Boston.

The PRESIDENT in the chair.

The following papers were presented: —

Demonstration of Electrical, Optical, and Mechanical Apparatus for Instruction and Research. By Henry P. Bowditch.

On the Means of teaching Anatomy, illustrated by new Models and Specimens. By Thomas Dwight.

The following papers were presented by title: —

Contributions to American Botany: I. Additions to the Flora of Western North America. II. Descriptions of New Species of Plants collected in Mexico, chiefly by Mr. C. G. Pringle, in 1889 and 1890. By Sereno Watson.

Contribution from the Herbarium of Harvard University: Descriptions of New Plants, chiefly Mexican *Gamopetalæ*, collected by Mr. C. G. Pringle in 1889 and 1890. By B. L. Robinson.

Eight hundred and forty-second Meeting.

May 13, 1891. — MONTHLY MEETING.

The PRESIDENT in the chair.

The following papers were presented by title: —

On some Theorems which connect together certain Line and Surface Integrals. By B. O. Peirce.

On some Cases of Electrical Flow in Thin Conductors. By B. O. Peirce.

The Quantitative Determination of Arsenic by the Marsh-Berzelius Method, especially as applied to the Analysis of Wall Papers and Fabrics. By Charles R. Sanger.

On the Products obtained by the Action of Nitric Acid upon Bromtrinitrophenylmalonic Ester. By C. Loring Jackson and W. B. Bentley.

Note on Tribrommononitrobenzol. By C. Loring Jackson and W. B. Bentley.

On the Structure and Development of Choreocolax Polysiphoniæ, Reinsch. By Herbert M. Richards.

Professor Edwin H. Hall gave an exposition of his thermoelectric method for the study of cylinder condensation in steam-engines. The apparatus, provided for by an appropriation from the income of the Rumford Fund, was exhibited.

AMERICAN ACADEMY OF ARTS AND SCIENCES.

Report of the Council. — Presented May 26, 1891.

BIOGRAPHICAL NOTICES.

Henry Jacob Bigelow	By Oliver Wendell Holmes.
Charles Otis Boutelle	Edward Goodfellow.
Alfred Hosmer	Henry W. Williams.
George Bancroft	A. McFarland Davis.
Julius Erasmus Hilgard	O. H. Tittmann.
Christian Heinrich Friedrich Peters	Arthur Searle.
Charles John Maximowicz	Sereno Watson.
Karl Wilhelm von Naegeli	William G. Farlow.
Eduard Schönfeld	Arthur Searle.

Notices of William Prescott Dexter, John Charles Fremont, John Le Conte, and Joseph Leidy, must be deferred until the next volume.

REPORT OF THE COUNCIL.

Since the last annual meeting, May 27, 1890, the Academy has lost by death twelve members; — viz. four Resident Fellows, Henry Jacob Bigelow, Charles Otis Boutelle, William Prescott Dexter, and Alfred Hosmer; six Associate Fellows, George Bancroft, John Charles Fremont, Julius Erasmus Hilgard, John Le Conte, Joseph Leidy, and Christian Heinrich Friedrich Peters; and three Foreign Honorary Members, Charles John Maximowicz, Karl Wilhelm von Naegeli, and Eduard Schönfeld.

RESIDENT FELLOWS.

HENRY JACOB BIGELOW.

Henry Jacob Bigelow was born in Boston, March 11, 1818, and died in Newton, Mass., October 30, 1890. He was the oldest of five children of Jacob and Mary (Scollay) Bigelow. His father was distinguished in various branches of science and literature; he was a former President of the Massachusetts Medical Society, and a President of this Academy; a man of great ability, a leading practitioner in Boston during his long life, and especially memorable as the founder of Mount Auburn, the earliest of our garden cemeteries. His son inherited many of his father's qualities. After attending Mr. Thayer's school, which he entered in 1826, he joined the Latin School, then under the charge of Mr. Leverett. When Mr. Leverett left the Latin School and established one of his own, he followed his instructor, having among his schoolmates William M. Evarts and William W. Greenough. He entered Harvard College in 1833, graduating in 1837. "If he does not become a distinguished man," Dr. James Jackson is reported to have said of him, "it will be because Boston is not a large enough field for his ability."

Mr. Henry Lee writes an interesting account of the early years he and Henry Bigelow passed together, from the age of three until Mr. Lee left to go to college, a year before his companion. He describes his young friend as a slender boy, lithe and active, a good gymnast and dancer, and full of contrivances and ideas of all sorts. He had a rather remarkable facility for mechanical work, — took early to shooting, a taste which lasted to the later years of his life; he was also fond of bird's-nesting, with the usual knowledge, or rather more, of birds and their haunts and habits; like his father, he had a taste for botany, which came again very strongly in his later years. He was a fair though not remarkable scholar, through school and college.

He early showed his independence of character. There was a rebellion while he was in college, and anxious parents went out to look after their sons, — among them Dr. Jacob Bigelow, who remonstrated with Henry. The latter reminded him that there was a rebellion in his own day. "Yes," said his father, "but I have seen the folly of it." "Well, I want to see the folly of it too," was Henry's (characteristic) answer.

He graduated with respectable rank in 1837. After leaving college he had threatening symptoms of pulmonary disease, for which he went to Havana; but he was able to continue the study of medicine which he had already commenced, in the prosecution of which he went to Europe, passing his time chiefly in Paris, visiting London, more especially to hear the lectures of Sir James Paget. He took his medical degree at Harvard University in 1841, and entered upon practice in Boston. He had determined to devote himself to surgery, and soon found himself in active business.

In connection with Dr. Henry Bryant, he established a kind of surgical dispensary, which was the subject of no little comment and some harmless satire from unknown rivals, which amused him and his friends as much as it did any of the medical community.

He soon became known as an enterprising and aspiring practitioner, who was mapping out his own path, deterred by no fear of rivals, and not afraid of his critics.

First on the list of Dr. Bigelow's published writings stands a "Manual of Orthopedic Surgery," being a Boylston Prize Dissertation for the year 1844.

The Boylston Prize Fund was provided by the generosity of Ward Nicholas Boylston, a Boston merchant. Its two annual prizes of fifty dollars each invited the competition of the younger members of the medical profession, and the gaining of them was a favorable introduction of the young practitioner to the medical world and the general public. The question, or one of the questions, for the year 1844 was the following: "In what cases, and to what extent, is the division of muscles, tendons, or other parts, proper for the relief of deformity or lameness?" Dr. Bigelow did not confine himself strictly within the limits of the question, but extended his labor until it took the form of the Manual above mentioned, an octavo volume of more than two hundred pages. This was a systematic and lucid treatise, far beyond the ordinary standard of the annual dissertations in scope and completeness.

For more than thirty years — from 1849 to 1882 — he was Professor of Surgery in the Medical School of Harvard University. In 1847 he was appointed one of the surgeons to the Massachusetts General Hospital. During all this active period of his life, he published many important papers, bearing more especially upon, but not confined to, surgical practice. The following list is furnished by Dr. R. H. Fitz, at the close of his tribute to Dr. Bigelow at the memorial meeting of the Society for Medical Improvement.

A List of some of the more important of Dr. Bigelow's Contributions to Medical Literature.

Manual of Orthopedic Surgery. Boylston Prize Dissertation. 1845.

Fragments of Medical Science and Art. An Address delivered before the Boylston Medical Society. 1846.

Insensibility during Surgical Operations produced by Inhalation. Boston Medical and Surgical Journal. 1846.

On a New Physical Sign, a Clicking in the Throat. Boston Medical and Surgical Journal. 1847.

Anæsthetic Agents, their Mode of Exhibition and Physiological Effects. Transactions of American Medical Association. 1848.

Ether and Chloroform: a Compendium of their History, Surgical Use, Dangers, and Discovery. 1848.

On the Employment of a New Agent in the Treatment of Stricture of the Urethra. Boston Medical and Surgical Journal. 1849.

An Introductory Lecture. 1849.

Dr. Harlow's Case of Crowbar Injury to the Head. Philadelphia Medical Journal. 1850.

Notes from Clinical Lectures on Surgery. 1851.

Science and Success. A Valedictory Address. 1859.

Surgical Cases and Comments. Boston Medical and Surgical Journal. 1861.

Rhigolene, a Petroleum Naphtha for producing Anæsthesia by Freezing. Boston Medical and Surgical Journal. 1866.

New and Successful Operation for Ununited Fractures, with Cases. Boston Medical and Surgical Journal. 1867.

Nitrous Oxide Gas for Surgical Purposes in 1848. Boston Medical and Surgical Journal. 1868.

The Mechanism of Dislocation and Fracture of the Hip. Boston. 1869.

Medical Education in America. Address before the Massachusetts Medical Society. 1871.

Death by Chloroform and alleged Death by Ether. Boston Medical and Surgical Journal. 1872.

Alleged Death from Ether. Letter to the Editor of the British Medical Journal. Boston Medical and Surgical Journal. 1873.

Turbinated Corpora Cavernosa. Boston Medical and Surgical Journal. 1875.

The True Neck of the Femur: its Structure and Pathology. Boston Medical and Surgical Journal. 1875.

A History of the Discovery of Modern Anæsthesia: a Century of American Medicine. Philadelphia. 1876.

New Methods and Treatment of Extrophy of the Bladder and Erectile Tumors. Boston Medical and Surgical Journal. 1876.

Lithotrity by a Single Operation. American Journal of Medical Sciences. 1878. Boston Medical and Surgical Journal. 1878.

Rapid Lithotrity with Evacuation. 1878.

Litholapaxy. New York Medical Record. 1879.

Litholapaxy. Boston Medical and Surgical Journal. 1879.

Litholapaxy. Letter to the London Lancet. Boston Medical and Surgical Journal. 1879.

Litholapaxy: an Improved Evacuator. Boston Medical and Surgical Journal. 1880.

The Code of Ethics adopted by the Massachusetts Medical Society. A Minority Report. Boston Medical and Surgical Journal. 1880.

Remarks on Modern Lithotrity. Lancet. 1881.

Radical Cure of Umbilical Hernia. Boston Medical and Surgical Journal. 1882.

A Case of Disease of the Liver. 1882.

Lithotrity with Evacuation. 1882.

A Simplified Evacuator for Litholapaxy. Boston Medical and Surgical Journal. 1883.

A Radical Cure for Umbilical Hernia. Boston Medical and Surgical Journal. 1889.

Fees in Hospitals. Boston Medical and Surgical Journal. 1889.

An Old Portrait of a Surgeon. Boston Medical and Surgical Journal. 1889.

The second publication on the list is entitled "Fragments of Medical Science and Art." Under this head is printed "An Address delivered in 1846."

The great aim of this essay is to show the importance of the imagination in science. The "Numerical Method" of Louis was at that time looked up to, by the more ardent disciples of that admirable observer and teacher, as the master-key which was to unlock all the secrets of disease and its remedies. Observe all the facts in a case, in a hundred or a thousand cases; tabulate them, add, subtract, multiply, divide them, and the laws of pathology and therapeutics will come out in your sums and quotients as inevitably as a clerk's balance at the end of his account-book. Dr. Elisha Bartlett's "Philosophy of Medical Science," published in 1844, presented the Numerical Method in a form which might be thought to exclude the imaginative element, and reduce the man of science to a mere statistician.

Dr. Bigelow's essay was a vindication of the true office and the importance of hypothesis. To illustrate his argument, he appealed to the history of great discoverers and inventors, of Copernicus, of Kepler, of Newton. "I am aware," he says, "that this position, namely, that hypothesis is essential to the discovery of scientific truth, is not recognized by many philosophers, especially in medical science of the present day. Bacon himself, feeling that unfounded theory, gratuitous assertion, had been a stumbling-block to all preceding science, was led to attaching too exclusive value to facts. 'We must not imagine or invent,' he says, 'but discover the acts and properties of nature.'"

In the face of Bacon's proposition, in the presence of the champions of the statistical school of observers, Dr. Bigelow maintained effectively and convincingly the true office of that higher faculty, which, instead of counting columns of figures, sees, in virtue of its special gift of insight, the hidden relations between a few facts remote from one another to all appearance, but which, connected by an hypothesis, are often verified by large observation, and become a part of accepted knowledge or true science.

It was not so much the originality of the thesis maintained by Dr. Bigelow as the reasonable and forcible method by which he expounded and illustrated it, and the peculiar fitness of his choice of a subject at that particular time. He knew when to strike, as well as how to strike. One of the most distinguished of our Boston practitioners said to me that he almost regretted Dr. Bigelow's having given so much time to special practical points, instead of applying himself to the larger problems of medical philosophy. I would not go so far as that, remembering how much he accomplished in the improvement of mechanical surgery, and the amount of human suffering which his inventive genius has relieved; but, after reading this essay, one may be pardoned for regretting that so good a thinker and reasoner was willing to allow his skilful handiwork to usurp so large a portion of his time and labor.

Had Dr. Bigelow left no other record. the association of his name with the great inventive discovery of artificial anæsthesia would preserve his memory to the latest period of civilization. On the evening of November 2, 1846, he called at my house in Charles Street with a paper which he proposed reading at the meeting of the American Academy of Arts and Sciences, to be held the next day, and which he wished me to hear. He began by telling me of the successful use of the inhalation of a gas or vapor which produced insensibility, during which a capital operation had been performed at the Massachusetts General Hospital. He was in a state of excitement as he spoke of the great discovery that the gravest operations could be performed without the patient's knowing anything about it until it was all over. In a fortnight, the news of this wonderful discovery, he said, will be all over Europe. He then proceeded to read to me the paper he had prepared, — the first formal presentation of the subject to the scientific world. The following is the official report, copied from the records of the Academy: —

"November 3d. 1846.

"Dr. Henry J. Bigelow read a paper giving some account of the new method of inhalation employed by Dr. Morton of this city to produce insensibility to pain during the performance of operations by the dentist and the surgeon."

No person took hold of Dr. Morton's discovery with such far-seeing. almost prophetic appreciation as the young surgeon who had been but a few years in practice, and who threw all the energy and ardor of his early manhood into his advocacy of the new and startling innovation which was destined to change the whole aspect of surgery. It was not merely by his sagacious foresight that he recognized the importance of this epoch-making novelty, but throughout its subsequent history. until its universal acceptance. he was the foremost champion of the claims of artificial anæsthesia. After the use of chloroform was introduced Dr. Bigelow remained faithful to the original anæsthetic agent. and was always ready to battle in the cause of ether as against chloroform, which. though more convenient, and in many cases useful, is a more dangerous agent than the other. His writings on this subject extend through a period of thirty years, from 1846 to 1876.

In the year 1850 Dr. Bigelow published a remarkable article on a case which may be considered on the whole as the most extraordinary in the annals of surgical injury. This was the famous "crowbar case," the account of which seemed to many incredible, and its mechanism beyond explanation. The story was briefly this. A man was ramming down a charge of powder in a hole drilled in a rock, when the charge exploded, and the tamping iron — a short round bar — was driven up through the side of his face, out at the top of his head, breaking upward through the top of his skull as if it had been pie-crust, shooting up into the air, and falling at some distance. Dr. Bigelow accepted the story as true, and undertook to show how the bar could have found its way up and out through the bones of the face and skull, traversing the brain, and cutting one of the optic nerves on its way. He prepared a skull to illustrate the course taken by the implement. The subject of this extraordinary accident lived many years, but an opportunity was found to inspect the injured parts after death, and Dr. Bigelow's explanation of the accident was fully confirmed.

In the midst of his scientific researches Dr. Bigelow never forgot the practical aim and end of the healing art. He cared quite as much for "common sense" in a medical man as he did for scientific acquirements; indeed, he rather undervalued pure science as compared with practical skill. His lectures are eminently practical, and most of his scientific researches tend to some important curative purpose. No man knew better than he what were the needs, and what should be the training, of the young practitioner who would make his way in the world; and his Lecture on "Science and Success" gives some of the best results of his wise experience.

In 1869 he published his essay, "The Mechanism of Dislocation and Fracture of the Hip." This subject had been long and diligently studied by the great surgeons of the past, more especially by Sir Astley Cooper. Dr. Bigelow threw new light upon the whole matter. I have requested Dr. Richard M. Hodges, who knew the history of Dr. Bigelow's researches more intimately than any other of his pupils and assistants, to make a brief statement of the leading points of his doctrine and practice in dislocations of the hip. The following is his answer to my request: —

"*Hip Dislocations.* — Although Winslow and Weitbrecht had described the two fasciculi of the ilio-femoral ligament, or ligament of Bertin, Dr. Bigelow first drew attention to the great strength of the anterior part of the capsule of the hipjoint, and defined with precision the two bands of the abovenamed ligament, diverging like the branches of an inverted Y.

"Dr. Bigelow showed that, so long as it remained unbroken in one or both of its branches, the Y ligament dominated all the dislocations of the hip joint with established features, and that it was the chief obstacle to reduction; the muscles playing only a subordinate and occasional part in giving position to the limb, or in hindering the reduction.

"Dr. Bigelow classified dislocations of the hip into regular and irregular.

"The regular dislocations, seven in number (four of them being new varieties), are those in which, one or both branches of the Y ligament being unbroken, the head of the femur is thereby held near the acetabulum, and their signs are constant.

"The irregular dislocations are those in which the Y ligament is wholly ruptured, and they therefore offer no constant signs. The head of the femur, being loosed from the acetabulum, is free to go anywhere.

"In the regular dislocations, manipulation of the Y ligament will alone effect reduction.

"The principle of this manipulation is flexion, which is efficient because it relaxes the Y ligament.

"The Y ligament being flexed, and therefore relaxed, the head of the femur is drawn or forced into the desired direction by 'traction,' which disengages it from behind the acetabulum and directs it toward the socket, — or by 'rotation,' which winds the Y ligament around the neck of the bone and so shortens it, thus compelling the head of the femur, as it sweeps around the acetabulum, also to approach the socket, into which it can be easily lifted.

"Dr. Bigelow converted random, ill devised, and fruitless movements into accurately conceived, instructed, and well directed manipulation."

Growing out of his investigations of this subject was his original study of the anatomical neck of the femur. By a series of parallel sections through the head and neck of the bone, he demonstrated the column or lamina of condensed bone in the midst of the cancellated tissue forming a line of support rendered necessary by the obliqnity of the neck of the bone.

In 1878 Dr. Bigelow published his essay, "Lithotrity by a Single Operation," of which Dr. Hodges speaks as follows: —

"*Rapid Lithotrity with Evacuation at a single sitting; or Litholapaxy.* — The normal urethra having been shown to admit instruments of greater size than surgeons had previously supposed possible, Dr. Bigelow constructed a lithotrite, improved in many of its details, (especially by devices which prevent the blades from clogging or becoming impacted with crushed material,) of a size much larger than had before been used. This permitted the attack of calculi exceeding in dimensions the limits previously thought allowable by crushing alone, i. e. without evacuation.

" Dr. Bigelow also constructed thin silver tubes, easy to be introduced, notwithstanding their large size (27–31 Charrière), through which evacuation of the crushed stone was made practicable by means of an elastic exhausting bulb of sufficient suction power to draw out the fragments previously comminuted to a size enabling them to enter and pass through the tube, — pulverization being no longer essential.

" Dr. Bigelow established the fact that with these instruments a sitting — two minutes having been, up to that time, assigned by Sir Henry Thompson as the proper average duration — could be prolonged, with the aid of anæsthesia, one to two hours, harmlessly for the patient and without detriment to the bladder. 'Lithotrity with a single sitting' has been shown to have a mortality less than that of 'Lithotrity with many sittings,' and it has entirely superseded the latter.

" The operation of Litholapaxy, at first supposed applicable only to adults, has been within the last few years extended in its use to children from two years of age upwards, with great success. They have never been supposed to come within the scope of old-fashioned lithotrity. This practice, adopted originally in India (Lahore), has latterly been introduced in England and America.

" Dr. Bigelow's invention may justly be said to have acquired a world-wide reputation."

I add a few words to this description by Dr. Hodges. He was led to think that a principal source of failure in that operation was the irritating effect of the fragments of stone allowed to remain in the bladder, which left it inflamed and sensitive, not in condition to be the subject of a second or third operation. If the bladder could be completely cleared at one sitting, this danger could be avoided. To effect this object, he designed new instruments, or modified such as were in use, so as to make them serve his purpose. He spared no pains in perfecting his apparatus. It is not to be supposed that his surgical innovations were at once accepted without question or opposition. The end of it all was, that his principal rival in the treatment of calculus, Sir Henry Thompson, became a convert to Dr. Bigelow's mode of dealing with stone in the bladder, and that this new method of operation is generally recognized as one of the great improvements of modern surgery. I myself had the opportunity of observing some of his experiments, and well remember the patient and persevering labor they involved. I recollect, more especially, the pains he took in getting plaster casts of the bladder and the urethra, and I learn from others that he bestowed the same care upon the instruments he contrived or adapted for the rapid removal of a calculus, by the method to which he gave the name of Litholapaxy.

Among Dr. Bigelow's other professional labors, I may mention his suggestion of a new refrigerant for producing local anæsthesia. This was brought forward in an article published in the Boston Medical and Surgical Journal, in 1866, under the title, "Rhigolene, a Petroleum Naphtha for producing Anæsthesia by Freezing."

A new anatomical observation was published by Dr. Bigelow in the same journal, in the year 1875, "Turbinated Corpora Cavernosa." The anatomical expert will recognize at once the analogy hinted at in this designation. The suddenness with which the air passage through the nostrils will become obstructed, and the equal suddenness with which it will be cleared, without the removal of any secretion, might well suggest the idea that some kind of erectile tissue was concerned in this familiar phenomenon. Dr. Bigelow examined the mucous membrane, and detected a spongy tissue with large cells, capable of being rapidly filled with blood and as rapidly emptied, — a structure resembling that of the corpora cavernosa, as the name he gave it implies. This is one of the very few additions to human descriptive anatomy which have been made in this country.

Dr. Bigelow was not a collector of books, nor a great reader. He opened a book as he would open a jackknife, to use it for some special purpose, which having accomplished, he shut it up and had done with it. I may be allowed to quote my own words, as they stand in the report of the memorial meeting held shortly after his decease by the Boston Society for Medical Improvement: —

"He read men and women as great scholars read books. He took life at first hand, and not filtered through alphabets. He was not ashamed of his want of erudition, and would ask questions on matters with which he was unacquainted with the simplicity of a child. But he would get what he wanted out of a book as dexterously, as neatly, as quickly, as a rodent will get the meat of a nut out of its shell. In the address before spoken of, on the use of imagination in science, he handled his rapidly acquired knowledge of the great authors he cited so like an adept in book lore that one might have thought he was born in an alcove and cradled on a book-shelf. He got what he wanted out of his authority, and the next day the volume he had eviscerated would be kicking about his floor, in the midst of the pamphlets, instruments, and all sorts of learned litter, which half covered his carpet. This power of finding what he wanted in the midst of rubbish he did not want, was hereditary. I remember Dr. James Jackson's saying to me, that, if there was a grain of wheat in a bushel of chaff, Dr. Jacob Bigelow would find it quicker than any man he ever knew."

Though Dr. Bigelow was not as much given to general reading as many less occupied professional men, it is not to be supposed that his active mind could fail to find subjects enough to interest it when not absorbed in some important investigation. He had many tastes and fancies which furnished him abundance of pleasant work, and called forth all his enthusiasm, each special pursuit in its turn. To this one object, whatever it might be, he gave himself enthusiastically for the time. When he had mastered all its details, when he had got at all its secrets, he left it for some new and inviting subject.

At one time he undertook the keeping and raising of fancy pigeons. For this purpose he established a columbarium at the top of his house in Chauncy Place, and showed his fantails and pouters, and other curious varieties, with great satisfaction, until he had learned their ways and become familiarly acquainted with their various graces and accomplishments. At another time his visitor would be startled by a most unceremonious address from a mino bird, to which he had taught certain phrases which could not fail to arrest the attention of his visitor. Another of his pets was a little bird which used to run up his sleeve in the most uncanny way. Between these two familiar spirits, he might well have been hanged as a wizard in the days of witchcraft. At another time he amused himself with the study of the ways of ants, placing the sand for their dwelling between two plates of glass, so that their operations could be observed. Again, he found his recreation in the royal handicraft of the locksmith, and studied the intricate contrivances of Bramah and Hobbs as he has studied the arrangements of the hip joint. With this fondness for animal life it is not strange that he held in great aversion the too frequent abuse of vivisection. I have often heard him express himself very strongly on this subject. I think his longest and strongest fancy was for paintings. He did not care to refer to the fact that he was color-blind, so far as the difference between red and green was concerned. When he was a boy he could not distinguish between the color of cherries and that of the leaves of the tree. Still, he had a passion for a picture, and spoke with enthusiasm of the color of some that pleased him. A bright patch on an old canvas attracted him in a moment; he would wet his finger and rub off the dust as eagerly as a gold-hunter explores a pebble with shining yellow particles scattered through it. He bought a good many pictures, and it was generally for their color, rather than for any other excellences, so far as my observation has gone. Another of his hobbies, if I may call them so, was the study of agates. He made a large collection of them, and examined some points of their internal formation with great interest.

Dr. Bigelow was not in the habit of speaking of his health, but he suffered at various times from symptoms of different kinds. The earlier pulmonary symptoms, which have been referred to, do not appear to have troubled him after the period of early manhood.

A few years before his death he was thrown from a vehicle, and received a blow on the head, which was followed by what seemed to be an inflammation of some of the membranes of the brain, leading to what he thought and what proved to be some thickening of the dura mater. His fatal illness seemed to be entirely disconnected with the injury referred to. Occasional passages of gall stones, inflammation of the bile ducts extending to the liver, and producing abscesses, with other marks of internal inflammation, inability to take food without extreme suffering, ended in gradual failure of bodily strength, the mind remaining bright and clear to very near the close of life. It was noted, in examination of the brain, that its convolutions presented an unusual complexity, suggesting a greater amount of vesicular matter than is common.

Dr. Bigelow wrote upon various important subjects of a more general nature. In 1871 he delivered an address upon medical education in America, before the Massachusetts Medical Society. In 1880 he wrote a minority report upon the code of ethics adopted by the Medical Society; and in 1889, an article upon fees in hospitals, in which he took strong ground against certain practices alleged to have grown up in some of these institutions. The last paper on the list of his works is entitled, "An Old Portrait of a Surgeon." A painting was presented many years ago to the Society for Medical Improvement, supposed to be a portrait of the great surgeon, Ambroise Paré. The truth of this supposition had been questioned, and remained undecided for thirty or forty years, when Dr. Bigelow thought it was time to settle it authoritatively. For this purpose he instituted the most searching inquiry; had photographs taken of numerous portraits bearing on the question; carried on a correspondence with experts in Europe; and finally established beyond doubt the fact that the portrait was not of Ambroise Paré, but of another practitioner of a certain reputation, but by no means so great a name as the illustrious surgeon's of whom it had been thought to be a likeness.

Dr. Bigelow was, unquestionably, a man of true genius. Sagacity in divining the truth; the power of continuous, patient, and searching investigation; inexorable determination to have the truth, if nature could be forced to yield it, characterized his powerful intelligence. The record of his printed publications is not a very long one, but it is weighty with original thought and practical discovery. He inherited a distinguished name, and his labors have rendered it memorable and illustrious, — one of the brightest in the annals of American surgery, — not to claim for it a still higher place in the history of the healing art.

Dr. Bigelow was married in 1847 to Susan, daughter of the Hon. William Sturgis. She died on June 9, 1853. One son, William Sturgis Bigelow, survives his parents.

CHARLES OTIS BOUTELLE.

Charles Otis Boutelle was born in Lexington, Massachusetts, August 4, 1813. His grandfather was an officer who served honorably throughout the Revolutionary War. His father, a skilful physician and a man of brave and earnest temperament, was a surgeon in the Navy during the war of 1812. His mother, a daughter of General Nathaniel Goodwin, of Plymouth, who served also during that war, was a woman loved and revered by all who knew her. She lived to nearly the age of one hundred, and her son never ceased to mourn her loss.

With such ancestry, many features of Mr. Boutelle's character can be traced to their source. Having while yet at an early age lost his father, he was educated by his uncle, the Reverend Ezra Shaw Goodwin, of Sandwich, Massachusetts, and received from him a thorough training in both the classics and mathematics. It soon became necessary for him to earn his own living; so he taught school, studied surveying, and one day, having heard that a friend who owned a work on that subject was willing to lend it to him, he walked twenty miles to get it. His skill in practical surveying soon became known, and a place was given to him on the survey of his native State by its director, Simeon Borden.

Having served creditably as Mr. Borden's chief assistant, he was appointed by Alexander Dallas Bache, Superintendent of the U. S. Coast Survey, to a position upon that work, in January, 1844. His service was at first in the office, but his active temperament and robust physique demanded less sedentary occupation, and his special capabilities for the field were quickly recognized by his distinguished chief. His advancement was rapid. In 1846 he was made an assistant in the Survey, and from that time forward gained steadily in standing on the work, being intrusted with the charge of important operations, which he conducted with his accustomed energy, and with the professional skill and fertility of resource always at his command.

For some years he carried on the reconnoissance for the primary triangulation upon the coast of Maine. He made the reconnoissance and selection of sites for three primary base-lines, and had personal charge of the measurement of a primary base-line (the Atlanta base) in Georgia. This measurement was three times repeated as a test of accuracy, the line being measured twice in winter and once in summer, with an accordance of results so close that the greatest divergence did not exceed a millionth part of the whole length of nearly six miles. He conducted the primary triangulation which was carried from the Atlanta base northward and northwestward along the Blue Ridge, to connect with the primary triangulation which was advancing southward and southwestward from the Kent Island base, and had charge of the surveys upon the coasts of South Carolina and Georgia.

During this period the bent of his mind was shown by the improvements he introduced into the methods and processes of the work; among these may be mentioned the form of preliminary base apparatus described in the Coast Survey Report for 1855; his form of tripod and scaffold observing signal, 1855; his experiments with lights for geodetic night signals, carried on for several years, and brought to a successful termination in 1880 by the adoption of the magnesium lights and the student-lamp reflectors.

In 1884 the charge of the Coast and Geodetic Survey office was assigned to him, and after his relief from that duty he was placed in immediate supervision of geodetic operations in the States which had organized their own geological and topographical surveys.

For a number of years he was a member of the board of commissioners for the improvement of the harbor of Norfolk.

On February 16, 1884, soon after taking up his residence in this city, he was elected a member of the Philosophical Society of Washington.

No notice of Mr. Boutelle's life would be complete that should omit reference to the important services which he rendered to his country at a critical period of its history. In common with the great majority of his brother officers assigned to duty with the military and naval forces, he participated in the hardships and dangers of the civil war. Soon after the outbreak of hostilities he was assigned to the command of the steamer Vixen and schooner Arago, as hydrographic officer of the South Atlantic Squadron, serving under Admirals Dupont and Dahlgren, and Commodore Lanman, U. S. N. This duty lasted throughout the war, and it devolved upon him the responsibility for the safety of navigation of the squadron along its entire cruising ground. With what patriotic devotion and professional ability this service was rendered, the records of the civil war amply attest.

Admiral Dupont, in his report to the Navy Department of the capture of Port Royal, refers to the fact that all aids to navigation had been removed by order of the Confederate authorities, and acknowledges the able assistance of Captain Boutelle in sounding out and buoying the channel, and thus enabling the squadron to advance to the attack.

General W. T. Sherman, U. S. Army, commanding the land expeditionary force, concludes a report, dated November 8, 1861, as follows: "It is my duty to report the valuable services of Mr. Boutelle, assistant in the Coast Survey. . . . His services are invaluable to the army as well as to the navy, and I earnestly recommend that important notice be taken of this very able and scientific officer by the War Department."

Personally, Captain Boutelle (as he was known to his friends after the civil war) was a man of varied reading and a most retentive memory, genial and witty in conversation, of uniform kindness of heart, and of a generous and hospitable nature, always assuming that others were guided by motives as unselfish as his own.

He combated manfully the advances of age and the inroads of disease, and it was not until the approach of his seventy-eighth year that, yielding to the solicitations of his family and friends, he sought relief from active duty. He died on the 22d of June, 1890, at the home of his son, Dr. Boutelle, in Hampton, Virginia.

ALFRED HOSMER.

Alfred Hosmer, of Watertown, Massachusetts, a Fellow of the Academy from 1879, was born at Newton, September 11, 1821, but removed with his mother to Walpole, New Hampshire, when nine years of age. Notwithstanding the limited opportunities for education afforded by a small country town, he qualified himself for admission to Harvard College, where he graduated with honor in 1853, and received his degree of M. D. in 1856. He spent nearly a year of study in Europe before beginning the practice of his profession at Watertown, where he soon gained reputation as a worthy successor of his uncle, Dr. Hiram Hosmer, a physician and surgeon of great repute. From this time until his last illness he enjoyed in an exceptionally high degree the confidence of the community in his own and the neighboring towns, and won the respect of his *confrères* by his untiring energy, accurate observation, sound judgment, fertility of resources, and unswerving fidelity to every duty.

Soon after his establishment at Watertown he married Helen Augusta, daughter of Josiah Stickney, Esq., and she, a daughter, and a son survive him.

Dr. Hosmer's published papers were marked by originality and independence, by alertness in discerning the presence of unusual features in disease, and readiness and good judgment in the adaptation of suitable means to the existing circumstances.

Dr. Hosmer was President of the Middlesex South District Medical Society; President of the Boston Obstetrical Society; and for many years a Councillor of the Massachusetts Medical Society, and was its President in 1882 and 1883.

Exceptionally brilliant as was Dr. Hosmer's professional career, this by no means included all of his public service. His vigorous activity and faithfulness were conspicuous in the affairs of citizenship, as well as in the duties of his chosen vocation. Among the offices of honor and trust to which he was for many years re-elected by his fellow-townsmen, he was a member of the School Committee, Trustee of the Public Library, Trustee and President of the Savings Bank, and President of the Watertown Historical Society. He was for many years surgeon of the United States Arsenal at Watertown.

Through the influence of the Massachusetts Medical Society, the Legislature of the State, during the administration of Governor

Rice, abolished the corrupt and inefficient coroners' system, and substituted therefor a carefully selected corps of skilled medical examiners, appointed by the Governor for a long term, and, happily, continued in office in most instances by reappointment; so that the State, the judicial authorities, and the people retain the advantage of experience as well as of ability in these chosen experts. No event in our time has contributed so largely to the honor of medicine and to the safety of the community as the creation of this body of skilled and trained officials, which has worked so intelligently and faithfully for the promotion of justice in the protection of the innocent and the disclosure of guilt. Great credit was due the Governor for his just appreciation of the importance of the proposed innovation, and for his judicious selection of the appointees, on which its success would so largely depend. Dr. Hosmer was appointed Medical Examiner for the District of Middlesex County, in which he resided; and upon the organization of the Massachusetts Medical Legal Society, composed of the seventy or more Examiners of the Districts of the Commonwealth, he was elected its first President, and by his zeal and executive ability greatly promoted the triumphant issue of this eventful experiment. Thanks to the high character and talents of Dr. Hosmer and his associate examiners, Legal Medicine has been recreated in Massachusetts, and the new system has been adopted in other States, as a long desired efficient auxiliary of public justice.

On the 29th of December, 1888, in returning from professional visits, Dr. Hosmer had an attack of cerebral hemorrhage. From this he largely recovered, although he continued to have some disability to find the desired words when conversing; but on May 14, 1891, after a few days' illness, he suddenly expired from rupture of the thoracic aorta, which, as well as the entire arterial system, was found at the autopsy to be extensively degenerated.

ASSOCIATE FELLOWS.

GEORGE BANCROFT.

George Bancroft was born at Worcester, October 3, 1800. He was the son of Aaron and Lucretia (Chandler) Bancroft. His father was the leading clergyman of the Unitarian denomination in Central Massachusetts; was honored with the degree of D.D. by his Alma Mater, Harvard College; was the author of a standard Life of Washington which has been republished in England and has also been recently reprinted in this country in popular form; was Vice-President of the American Antiquarian Society for many years; was President of the American Unitarian Association from its organization in 1825 to 1836; and was a Fellow of the American Academy of Arts and Sciences. His mother was a daughter of Judge John Chandler, and was a recognized leader among the women of the little town in which her lot was cast. Her time during married life was engrossed in the care of a large family of children, who were reared in a manner suited to their social position, with no other income ordinarily at command than her husband's salary as a country clergyman, eked out by such increase as could be obtained from teaching the children of parishioners. The lesson of George Bancroft's boyhood was that he must rely for his future support upon himself alone.

A sister of Mr. Bancroft married John Davis, the greater part of whose life was spent in public service, as Governor of Massachusetts, Representative in Congress, or United States Senator. A nephew, J. C. Bancroft Davis, succeeded Mr. Bancroft at the German Embassy. The present Chief Justice of the United States finds a common ancestor with Mr. Bancoft, one generation back of the historian's father.

It was Dr. Bancroft's earnest desire that his son should adopt his own profession; and, in preparation for that career, George was sent to Harvard College, where he graduated in 1817, second in his class. The opportunity was then offered him to complete his studies in Europe at the expense of the College. Of this he gladly availed himself, and the next five years of his life were spent in study and travel in Europe. He studied at Göttingen and Berlin, taking the degree of Ph.D. at Göttingen before he was twenty years of age.

This period of his life was rich in friendships of distinguished men belonging to a generation now passed away. It was fraught with benefits to him in his future career. The familiarity with the German language which he then gained was of incalculable service to him, both in his diplomatic and in his literary labors. The philosophic cast of his studies somewhat influenced his methods of thought, and found sufficient expression in his writings for his critics to charge him with mysticism. Yet their tendency was to raise his strong, nervous personality above the plane of prejudice, and to help him to measure events upon a just standard. The estimate in which he was then held may be judged by the language in which Humboldt introduced him to Pictet. Bancroft was described by Humboldt as a "young American, who has made an excellent study of philosophy and philosophic history in Germany." His reception at this time by prominent men in the world of European letters doubtless inspired in him the confidence which was required when, a few years later, he concluded to undertake what was to prove the work of his life.

The privilege of study in Europe had been afforded him by Harvard College, with a view to his thus preparing for a professorship in that College when there should be a vacancy. So far as his immediate prospects were concerned, he had not on his return to the United States, in 1822, ultimately abandoned his intention of adopting the profession of the Christian ministry; and he did in fact preach in his father's pulpit, and from time to time elsewhere, for a brief period. He was appointed Tutor of Greek at Harvard College in 1822, and filled that office for a year.

From 1823 to 1830, his time was devoted to teaching at Round Hill School, Northampton. In 1827 he married Sarah H. Dwight. She died in 1837. By this marriage he had two sons and one daughter. The sons survive their father. In 1838 he married Mrs. Elizabeth (Davis) Bliss, who died in 1886. She bore him one daughter ,who died while yet a child.

It was while connected with Round Hill School that he launched his first literary venture, a volume of poems, published in 1823. His pen during this period of his life was also busily at work upon translations from the German, and on articles for the prominent reviews of the day. An oration delivered on the 4th of July, 1826, and published the same year, in which he announced the democratic nature of his political views, and a pamphlet on "The Bank of the United States," published anonymously in 1831, indicate the interest he took in the political questions of the day. In 1830 an opening was afforded him through which he might have entered political life if he had cared to do so. He was elected to the legislature, but declined to take the seat. Next year he was tendered the nomination to the Senate, but, notwithstanding the fact that his election would have been certain, he declined the honor.

In 1834 he published the first volume of his History. "I have formed the design," he says in his Preface, "of writing a History of the United States from the discovery of the American Continent to the present time." It will be seen that he did not attempt to carry out the plan as thus promulgated. History requires the aid of intervening time as a guaranty that the writer shall escape the prejudices and passions provoked by current events. It was impossible that Mr. Bancroft should treat with uniform impartiality of men and affairs belonging strictly to the past, and of events which had been shaped by the generation then controlling the destiny of his country. His History, as published, concludes with the establishment of a constitutional government in the United States, and to its production he devoted the remainder of his life, publishing from time to time the several volumes of the series, as intervals of leisure in his political and diplomatic labors permitted.

In 1835 he removed to Springfield, and next year ran for Congress in that district on the Democratic ticket, but was defeated. From 1838 to 1841 he was Collector of the Port of Boston. In 1844 he was Democratic candidate for Governor of Massachusetts, but failed of election. In 1845 he was Secretary of the Navy under James K. Polk, and while he held that position he founded the Naval School at Annapolis. The need of a training school for naval officers similar to that at West Point for the Army had long been felt. The usual sectional jealousies and political prejudices which impede useful legislation at Washington were to be apprehended if a direct appeal for the establishment of such an institution were made. An opportunity offered to secure the post at Fort Severn, Annapolis, without legislation. Existing laws permitted the stationing of certain officers and instructors at this post. It was also possible to detach midshipmen from vessels as they arrived in this country and order them to Annapolis. All of this was accomplished. Orders for the establishment of the school were issued, and a scheme was promulgated which, in 1846, was published at Washington, under title of "Plan and Regulations of Naval School at Annapolis." The school was formally opened October 10, 1845. On the 1st of January, 1846, its membership was composed of forty-nine midshipmen and seven acting midshipmen. The Navy thus became indebted to Secretary Bancroft for a training school.

While Secretary of the Navy, he issued the order to take possession of California in the event of a war between the United States and Mexico, and while acting as Secretary of War, during the temporary absence of Marcy, Bancroft issued the order to General Taylor to march into Texas.

The stirring events in which Bancroft as a member of Polk's Cabinet participated were of momentous consequence to his country. Every believer in what was then termed the "manifest destiny" of the country was compelled to admit that it was true statesmanship to seize the opportunity for gaining the magnificent territory offered for our control by the republic of Texas. Every antislavery man felt that Texas would not have been annexed, except that it would add another slaveholding State. Whether to sacrifice an opportunity which might not occur again, or to take the chances of a future adjustment of the powers of the two sections, was the question which antislavery men were forced to solve. To most Northerners the overwhelming antislavery sentiment in the North made the solution of the problem easy; but to an antislavery Democrat holding an office of power, the position was a difficult one. Mr. Bancroft was a Democrat, an ardent lover of his country, and an antislavery man. Rev. Dr. Hale is authority for the statement that, while his confirmation as Secretary of the Navy was before the Senate, he was approached by a Senator on the subject of slavery, and in reply to questions as to his views he said that he was an antislavery man, and if he were to go through the Senate he must go erect and not on his knees. The annexation of Texas carried with it a possibility of war with Mexico. The general opinion at that time was that the days of Mexico's occupation of Upper California were numbered, and it was feared that England would take possession whenever opportunity offered. That it would be in the interest of civilization if the United States should by any chance secure this territory, there was no doubt in any person's mind. It was under these circumstances that Bancroft, to quote the language of Von Holtz, "never wearied of impressing this one precept upon Sloat, Stockton, and Biddle. See to it that as soon as practicable Upper California at least be in our hands, in order that we may retain it if peace is concluded upon the basis of *uti possidetis.*" The same author measures the situation in the United States at that time in the following language: "After its territory had once been extended thus far to the West, it was a proper, nay, an inevitable thought, that its banner must overshadow the entire continent, in its whole extent from ocean to ocean."

In 1846, Bancroft was transferred from the Cabinet to the Court of St. James. During the three years that he remained in London as Minister Plenipotentiary, he negotiated a postal treaty between

Great Britain and the United States. He took great interest in the debates in Parliament on the Navigation Laws, and exerted his influence to secure a modification of their rigor.

When Bancroft went to London, he found that his History, three volumes of which had then been published, had made him a famous man. He was cordially welcomed in society, and was admitted to the friendship of the prominent literary men and statesmen of the day. "I met him everywhere," says Robert C. Winthrop, "and witnessed the high estimation in which he was held by literary men like Rogers, and Hallam, and Alison, and Milman, and Lord Mahon, and by statesmen like Peel, Palmerston, and Russell."

Under such circumstances the opportunity to consult original documents bearing upon the topics of his History were exceptional, and he availed himself of it to amass an amount of material such as no man working in the same field had before that time had at his command. While Minister to England, he received from the University of Oxford the degree of Doctor of Civil Law.

In 1849 he returned to the United States, and took up his abode in New York, where he devoted himself to historical labors. His life was one of great regularity. Each day had its appropriate hours set apart for labor, for exercise and recreation, and for social duties. He faithfully followed the allotted programme, thus securing the best results for mind and body. The fourth volume of the history — the first of the Revolution — was published in 1852, the fifth in 1853, the sixth in 1854, the seventh in 1858, the eighth in 1860, and the ninth in 1866. Besides these, he published in 1855 a volume of "Literary and Historical Miscellanies." In February, 1866, he delivered before Congress an oration in memory of Abraham Lincoln.

In May, 1867, he was appointed Minister to Prussia. He remained at Berlin until 1874, representing our government at this Court during its successive changes from the kingdom of Prussia to the North German Confederation, and finally to the German Empire. While Minister to the North German Confederation, he concluded naturalization treaties which included in their scope Prussia, Baden, Bavaria, and Würtemberg. These treaties were the first to recognize the right of a citizen to change his allegiance, and could only have been secured by a man of exceptional influence. While at Berlin, he presented the American case in the arbitration between Great Britain and the United States concerning the title to the island of San Juan. This act was performed by him under a separate appointment. The decision of the Emperor sustained the title of the United States, and finally disposed of the vexed question. In 1868, he received from the University of Bonn the degree of Doctor of Laws, and in 1870, on the fiftieth anniversary of his Doctorate of Philosophy at Göttingen, that University conferred upon him an honorary Ph. D. The circumstances connected with this event attracted much attention. Congratulations were showered upon the head of Mr. Bancroft in person, by letter, and by telegraph, from crowned heads, from learned societies, from generals, and from men of letters. Bismarck sent his from the field. Americans when they read the story of these events realized that rare honors had been heaped upon the head of their Minister.

In 1874 he was at his own request recalled. On his return to this country he divided his life between Washington and Newport, making the former place his winter, and the latter his summer home. Almost to the last day of his life, he continued his methodical habits, parcelling out his labors and his pleasures, allotting specific periods of the day to each, and rigidly adhering to his plan. Those who were present at the opening session of the American Historical Association in Washington, in 1886, will remember an incident which will illustrate the value he attached to punctuality. At the appointed hour he was ready to open the meeting, but owing to circumstances over which he had no control was unable to do so. As soon as he was able, he called the audience to order, saying, "I pray you all to bear witness that I was here, prepared to open this meeting, at precisely ten o'clock."

Volume X. of his History, which practically completed the work, was published in 1874. The Centenary Edition, revised and condensed into five volumes, was published in 1876. An edition was published in London in 1862, and a German edition in Leipzig in 1875. Perhaps these foreign editions did not have his personal supervision. Volumes XI. and XII. were separately published under the title of "History of the Formation of the Constitution of the United States," in 1882. A revised edition, which included the history of the Constitution, and which was termed by him the "final revision," was published in six volumes in 1883–85. The last volume which he published was a "Life of Martin Van Buren." The manuscript for this sketch had been prepared many years before. The last work actually given by him to the public was a trenchant criticism of the Supreme Court in the Legal Tender

Case. This was published in 1886, under the title of "A Plea for the Constitution of the United States of America, wounded in the House of its Guardians."

Allibone gives a list of his miscellaneous publications. The Annual Report of the American Historical Association for 1889 gives a list of his historical works, including papers communicated to historical societies. Still another list of his publications will be found in Appleton's Cyclopædia of American Biography.

The social position which Mr. Bancroft held when he returned from Germany to this country was enviable. His friendships comprehended the great men of two hemispheres for half a century. Learned societies at home and abroad had elected him to active and honorary membership. He bore honorary degrees from American, English, and German universities. A partial list of these societies and degrees occupies nearly half a column in the Quinquennial Catalogue of Harvard University. The Senate of the United States extended to him the unprecedented honor of free access to the floor of their chamber. His society was eagerly sought both at Washington and at Newport, and it required all the restraints of his methodical habits to preserve strength for the work still before him. Towards the end of his life the anniversaries of his birthday were made much of by friends. Flowers, messages, and congratulations were showered upon him. October 3, 1887, Browning cabled him as follows: —

> "Bancroft, the message-bearing wire
> Which flashes my all-hail to-day
> Moves slower than the heart's desire
> That what hand pens tongue's self might say."

He took great pleasure in the cultivation of roses; and the "George Bancroft" in the catalogues of rosarians bears witness to the recognition of this taste on the part of horticulturists. He was fond, especially during the latter part of his life, of riding; and visitors to Washington or Newport felt that they had missed one of the sights of the place if they had failed to see the slight, erect form of the historian, crowned with his snow-white hair and beard, as he took his daily exercise on horseback. He was grateful for the opportunities afforded him at Exeter, where he went to school, and founded there a scholarship. At Harvard he founded a fellowship which he named, after his old teacher, the "John Thornton Kirkland Fellowship." In honor of his parents, he placed in possession of the city of Worcester a fund for the maintenance of a scholarship which he called the "Aaron and Lucretia Bancroft Scholarship."

He died, January 17, 1891, at his home in Washington. His friends were not unprepared for the event, as he had been perceptibly failing for a long time. The Emperor of Germany caused flowers to be laid upon the casket which contained his remains. The funeral services were held at Washington; but the body of the historian was interred in the same cemetery in Worcester which holds the remains of his father and mother.

The position of Bancroft's History as the standard history of the United States has left for the critics to discuss only the question how long the work will be able to maintain this position. Allibone has grouped in his columns the opinion of a number of competent writers. A few extracts from these opinions expressed during the progress of the work, a brief analysis of some of the objections which have been made to the History itself, and a few quotations from later writers, in which they state their estimate of the work, will help to determine this question. Heeren, under whom Bancroft studied and who was his personal friend, reviewing the first three volumes, says, "We know few modern historic works in which the author has reached so high an elevation at once as an historical inquirer and an historical writer." Edward Everett, reviewing the first volume, says, "As far as it goes, it does such justice to its noble subject as to supersede the necessity of any future work of the same kind." Prescott, reviewing the third volume, says, "His Colonial History establishes his title to a place among the great historical writers of the age." Dr. Griswold in his "Prose Writers of America," treating of Volumes I., II., and III., thinks that "he becomes insensibly the advocate of the cause of freedom, which invalidates his testimony." The Edinburgh Review, on the other hand, says, "The real liberality, the general fairness, the labor and conscientious research it evinces, deserves, and we are assured will receive, his [the English reader's] warmest approbation." The Westminster Review predicts, "with confidence, that his work will be reckoned among the genuine masterpieces of historical genius." Lecky, in his "England in the Eighteenth Century," accuses him of violent partisanship, and charges that it greatly impairs his "very learned History." The foregoing will illustrate the reception of the History by literary men during its progress. It is difficult to conceive of tributes more gratifying to an author. If there had been no voice in England to raise the charge of partisanship against this ardent American while engaged in depicting the preliminary struggles of the Colonies with the mother country, it would have been because he had failed to accomplish what he had undertaken. If the English people, as a whole, had not been able to appreciate Bancroft's labor and conscientious research, his fairness of purpose, and the real liberality beneath his sharp, incisive criticism, it could only have been because they had become less tolerant than we know them to be.

In the composition of the first three volumes, which are devoted to Colonial History, Bancroft relied upon resources such as are at command of ordinary writers. "I have been most liberally aided," he says in his Preface, "by the directors of our chief public libraries; especially the library at Cambridge, on American history the richest in the world, has been opened to me as freely as if it had been my own." The period covered topics concerning which an expression of opinion did not necessarily raise a controversy. Believers in the historic value of the Sagas did not feel it their duty to attack one who accepted the visits of the Norsemen to this coast as a natural probability, because he thought the Sagas themselves mythological in form and obscure in meaning. The exercise of discriminating judgment as to the voyages of the period, while it might arouse criticism as to the accuracy of the adoption of this or that narrative, did not provoke acrimonious discussion. The wide difference between the reception of the earlier volumes, and of the series which bore upon Revolutionary topics, calls attention to the scheme of the History, and emphasizes the manner in which that scheme was developed. The whole History is divided into three parts: the history of the Colonies; the history of the Revolution, which in turn is separated by the Declaration of Independence into two subdivisions; and the history of the formation of the Constitution. The publication of the portion dealing with the Revolution stirred up a series of controversies. Bancroft was compelled to express himself frankly concerning men who had living descendants. Family pride was aroused, and pamphlets were issued in defence of ancestors whose reputations were supposed to have been injured by the strictures of the historian. Mr. Winsor, in a note in the eighth volume of the "Narrative and Critical History of America," gives an account of the literature of this description bearing upon the most important of these pamphlet battles. The controversies there recapitulated were based upon language used by Bancroft concerning Colonel Timothy Pickering, General Greene, General Schuyler, General Sullivan, and Joseph Reed. In the last case it was shown that Bancroft had been misled by an incident which had occurred to another Colonel Reed; and the charge based upon that error was withdrawn in the Centenary Edition of the History. The language used with reference to Schuyler and Sullivan was also in each case modified in this edition, but the judgments of the men remain substantially as before. In the Preface to the sixth volume, he says, "I hope at least it will appear that I have written with candor, neither exaggerating vices of character, nor reviving national animosities, but rendering a just tribute to virtue wherever found." It was in this spirit that he approached the subject; and upon the judgment of posterity as to how far he was able to live up to it his reputation as an historian must stand. The majority of readers at the present day will give him credit for the exercise of a judicial spirit in reaching the conclusions for which he was attacked. His History would be worthless if he had not been manly enough to express his opinions. His conclusions have seldom been doubted, save where they conflicted with the estimates of kindred.

His style has been condemned as redundant and pompous; but his capacity for marshalling events in narrative form has been admitted even by those disposed to criticise. Colonel Higginson's opinion on this point is vividly set forth in the following language: "The reader is compelled to admit that his resources in the way of preparation are inexhaustible, and that his command of them is astounding. One must follow him minutely through the history of the war for independence, to appreciate in full the consummate grasp of a mind which can deploy military events in a narrative as a general deploys brigades in a field." The same writer calls attention to a fault "which Bancroft shared with his contemporaries, but in which he far exceeded any of them, — an utter ignoring of the very meaning and significance of a quotation mark." This criticism is based upon an obvious defect, the existence of which cannot be denied. Instances can be found in Bancroft's works in which quotation marks are used enclosing paragraphs in which there were abridgments and insertions for the purpose of making the thought continuous, without the typographical marks essential to denote these changes. He does not, however, need especial defence for pursuing the practice of his contemporaries. It is logical perhaps to say that, when tried by Mr. Bancroft's literary methods, the mass of correspondence quoted in the History of the Constitution, "though valuable as suggestion, is worthless as authority," but it is severe. The same test would compel the rejection of Sparks's Washington, if indeed it would not carry with it the entire collection of Washington's manuscripts in the State Department; for we know that some of the letter-book copies of the correspondence on file in that office were revamped by Washington himself. There is no hesitation in quoting Sparks, and perfect confidence is felt that he made no change, either by alteration or omission, that could in his judgment affect the sense of the text, nor is it to be believed that Washington ever changed a word in his letter-books which he thought could modify their interpretation. The point must be indeed narrow and technical, a question of close construction or of the use of a word under circumstances demanding for an estimate of its value all that immediately precedes or follows it, that would call for the verification of any of Bancroft's quotations by comparison with original documents.

Marginal references in the first six volumes, although not copious, are frequently met with. In the seventh volume they are entirely omitted, and thenceforward through the History are rarely to be seen. This change is much regretted by students. An explanation of why the references were omitted in the seventh volume is to be found in the Preface. The reason stated was "the variety and multitude of the papers which have been used, and which could not be intelligently cited, without burdening the pages with a disproportionate commentary." It was apparently Bancroft's intention at that time to cull out for publication such letters as would confirm his narrative, "and possess an intrinsic and general interest by illustrating the character and sentiments of the people during the ten or twelve years preceding the 4th of July, 1776." This purpose he did not carry out.

The extracts from the opinions of reviewers previously quoted show that nearly all of the writers were of opinion that Bancroft was destined to hold permanently his position as the historian of the United States. How far the charges of partisanship made by such writers as Griswold and Lecky, and later by pamphleteers in this country, have affected this position, may be measured somewhat by the expressed opinions of historical students. Robert C. Winthrop, at the first meeting of the Massachusetts Historical Society after Bancroft's death, said: "You have well said, Mr. President, that Bancroft was foremost as the historian of the United States. His great work in all its varied editions will always be read and recognized as the leading authority on American history for the period which it includes. His style may be criticised, and censured as redundant or rhetorical. His philosophy may be discarded as partaking occasionally of that German mysticism which he imbibed in his youth. A vein of partisanship too, may sometimes be detected amid all his professions of impartiality. It could hardly be otherwise. No one in writing history, or in doing anything else, can escape from himself, or can wholly conceal, even should he try to do so, his own preconceived opinions, his own individual peculiarities and idiosyncrasies." Further on in his remarks Mr. Winthrop added, "The truth of history was uppermost in his aims and efforts from first to last." Two months later Mr. Winthrop attended the semiannual meeting of the American Antiquarian Society. Bancroft had for twenty years been the First Vice-President of this Society. A memorial of his life was read by Samuel S. Green. Mr. Winthrop, alluding to Bancroft's death, then said, "I do not forget that he and I shared so long the distinction of being the oldest members of the Society, and that is now left to me alone." He then added, with great earnestness of manner, "I paid my little tribute to him at our Massachusetts Historical Society, and I have nothing to add to it, and nothing to detract from it." Mr. Winsor, in the Narrative and Critical History of America deals with the question of the probability of Bancroft retaining his position in the following language: "His learning and the extraordinary resources of his material are likely to make his work necessary for the student, till another with equal or better facilities shall compass the subject in a way to gain wider sympathy." In other words, the writer who shall supplant Bancroft must command at least equal facilities, and deal with the subject in a more attractive way. To measure the probabilities of the occurrence of these events, it is necessary to review the resources at his command.

It has been seen that no especial claim can be made for him in regard to the facilities at his disposal for the preparation of his Colonial History. The researches of topical students have placed within easy reach of the writer of to-day much that was to be learned only by diligent study when Bancroft wrote. To examine the Colonial records of the original States, he was obliged to travel from State to State. Many of these records have since been published, and are now to be found in all the great libraries. When we reach the Revolutionary period, however, it is easy to comprehend why Colonel Higginson speaks of Bancroft's resources as inexhaustible, and why Mr. Winsor characterizes them as extraordinary. Bancroft himself has given a detailed recapitulation of his manuscript sources of authority in the Prefaces to his sixth and ninth volumes. There is not space at command to give this information in full. The following extract from Mr. Winsor's abridged statement of the information furnished by these Prefaces will serve to show how remarkable were his opportunities: —

> "Nothing was refused him in the English State Paper Office, nor at the Treasury. The manuscripts of the British Museum and the Royal Institution, such of the Chatham Papers as had not been printed, the Shelburne Papers, including the letters of Shelburne and the King, an autobiography of the third Duke of Grafton, a journal of the Earl of Dartmouth, the letters which passed from the King to Lord North, not to mention others of lesser importance, were placed at his disposal. In France the archives were thrown open to his search without restraint, and the treasures of the Marine and War Departments were largely drawn upon. On the negotiations for peace, the French archives offered him the richest material. From Germany his acquisitions were peculiarly valuable, as Sparks had scarcely reaped anything from that field. He found the archives of Hesse-Cassel closed to him as to others, but through the instrumentality of Friedrich Kapp and others he secured the possession of private journals and reports of the Hessian officers, and caused searches to be made in the wide field of the contemporary publications in Germany for letters and criticisms on the part of the German auxiliaries in the war which he considers 'in the main the most important of all that have been preserved.' From Berlin, he got the reports made to the Duke of Brunswick by his officers which have finally found a lodgment in the Russian archives; and he also secured the collection which Max von Eelking, the writer on the Hessian story, had amassed in his studies. He likewise obtained copies of the correspondence of Frederick the Great with his foreign ministers, so far as it touched upon the affairs of America. From Moscow and Vienna, from Holland and from Spain, other documents came to swell the record, which have enabled him to make his account of the foreign relations of the Confederacy the best by far which had been prepared.
>
> "His wealth of American papers is probably from their scope unsurpassed in private hands. He had of course at his command the resources of the government archives, and those of the original States; he could examine the papers of the Revolution gathered in public libraries, and in the cabinets of historical societies; and besides these he had his own gatherings; the correspondence of the agents of the various Colonies in

London prior to the outbreak of actual war, like Bollan, Jasper Mauduit, Richard Jackson, Arthur Lee, Franklin, W. S. Johnson, and others; the papers more or less extensive of Hutchinson, Israel Mauduit, Pownall, Hollis, Mayhew, Andrew Eliot, Colden, Bernard; and, above all, the papers of Samuel Adams, which passed into Bancroft's hands some years ago.

"He speaks also of two volumes of papers of Greene, and the papers of Anthony Wayne, which were submitted to his inspection."

If ever the opportunity should occur for one man to command such resources as these, he still must, in the contest for supremacy, measure swords with Bancroft in the treatment of the subject.

Mr. Winsor in the "final statement" in his History speaks of the value of monograph, as rounding the treatment of any phase of history in a way rarely accomplished in more comprehensive work. One of the criticisms which has been made upon Bancroft's work is that he did not keep up with the times, and that in his last revision he did not devote himself to a more detailed investigation of the work of specialists in the several topics covered by his History, in preference to confining his labor mainly to the elimination of redundancies and the condensation of material. A glance at the manner in which he carried the scheme of his History into execution will furnish a partial answer to this criticism. He treated his subject by topics exhaustively, and as he progressed he devoted his time to the investigation of the new field which was before him. It was impossible that he should be constantly at work where he had already concluded his labors, and equally impossible but that from time to time his attention should be called to errors which notwithstanding his vigilance had crept in. As edition after edition of his works came out, he eliminated such errors as came under his observation; but his main labor was devoted to the perfection of his scheme. When the History proper was concluded, and afterward when the volumes on the Constitution were published, he was confronted with the question, whether, in a revision of the published volumes, he should merely try to condense them, or whether he should attack the subject anew and attempt to treat it as a whole, taking up the study of each part where he had previously dropped it. At his time of life the latter course was practically impossible. He chose the former, and, while opinions may differ as to the wisdom of the choice, it will commend itself to the majority.

Mr. Bancroft's career has been presented as statesman, as historian, and as citizen. Whether his memory is longer to be preserved through his founding the Naval School, and through his connection with the acquisition of California and the enlargement of the rights of naturalized citizens, in the first capacity; through his recognized pre-eminence as the historian of his country; or through the grateful recognition of his forethought in founding exhibitions at Exeter, Harvard, and Worcester, posterity alone can tell.

JULIUS ERASMUS HILGARD.

The father of the subject of this sketch was a man of brilliant mind and of high attainments. He gave up a promising judicial career in Bavaria, against the wishes of that government, because of his republican sentiments, and of his desire to find a congenial sphere of action in the ideal republic which he expected to find on this side of the ocean. Accredited to the good will of the American people by a letter of introduction from Lafayette, he emigrated to this country with a large family of children, and arrived at New Orleans in the winter of 1835. Going up the Mississippi, he purchased a farm near Belleville, St. Clair County, Illinois, and there devoted his time to farming and to the education of his children, when the latter were not engaged in the manual labor inseparable from a pioneer life in the West. His son Julius, born in Zweibrücken, January 7, 1825, received from his father instruction in the classics and in the modern languages, but soon outstripped his teacher in mathematics, and at the age of eighteen went to Philadelphia to study engineering. There, at the house of a mutual friend, he met Professor Bache.

In tracing the history of his connection with the Coast Survey, to which his life was devoted, we find a letter from young Hilgard to Bache, dated January, 1844, calling the attention of the latter to errors in the formulas used by the Coast Survey in the computation of geographical positions, and giving his own development of correct formulas. In reply, Superintendent Bache wrote to the youth of nineteen, saying, "You have overriden two of our most experienced computers, and have shown that they were seriously in error." To an offer from Bache of employment in the Survey in a subordinate capacity and at small pay, he responded that he would rather do "high work at low pay than low work at high pay," and gladly accepted the position. He entered at once upon his duties, but his formal appointment was dated December 28, 1846. His ability as a field officer in astronomical work and triangulation at once secured him the commendation of his immediate superiors and of the Superintendent. In 1851, 1852, and 1853 he was in charge of the computing division, and there again his ability was made manifest, as is shown by the report of Captain Benham, U. S. Eng., who, on assuming charge of the Coast Survey Office in 1853, reported to the Superintendent that he found the computing division the best organized division in the office.

The annual reports of the Survey contain the evidence of Hilgard's scientific activity up to 1861, when for a brief period he severed his direct connection with the Survey to embark in private enterprise. But at the outbreak of the War, when the very existence of the Survey was endangered by threatened legislation, Bache appealed to him to return to Washington and help save the Survey. Responding at once, Hilgard called upon Schuyler Colfax and Roscoe Conkling, eminent as leaders in the dominant party, and made a strong argument showing how necessary such an organization as the Coast Survey must be to the country in time of war. So searching was Roscoe Conkling's examination of Hilgard's argument that the latter mistook his earnestness for an evidence of a spirit hostile to the Survey; but to his relief and satisfaction it was soon shown that he had found a most earnest supporter in Conkling no less than in Colfax. This incident is here recorded in order to recall to the mind that, in summing up the labors of Hilgard in the cause of science, it should be remembered that it is a sufficient outcome of a life to have borne a large part in maintaining the efficiency of so great and useful an institution as the Coast Survey. In 1862, Hilgard assumed charge of the Coast and Geodetic Survey Office, and this during the war involved heavy responsibilities.

Professor Bache having become incapacitated through mental disease, the duty of directing the Survey in all its branches devolved upon Hilgard in the autumn of 1864, in addition to his labors as assistant in charge of the office. Thus he was virtually Superintendent until the appointment of a successor to Bache, in February, 1867, without reaping the reward of a formal appointment, which he richly deserved. As an estimate of his services by a critic by no means partial, and yet competent, the opinion of Bache's successor, Benjamin Peirce, is cited here: "During the illness of my lamented predecessor, the administration of the Survey fell upon the shoulders of the assistant in charge, J. E. Hilgard. The distinguished ability with which this difficult service was discharged was manifest to all. He has extended to me the benefits of this experience liberally and loyally. While I willingly acknowledge myself under deep and lasting obligations to him for the aid thus rendered me, I can also testify that in all respects he has been equally true to my predecessor, the greatness of whose reputation has not been diminished in his keeping."

Until his appointment to the superintendency, in 1881, Hilgard continued in charge of the Coast Survey Office. In addition to this duty, he virtually conducted the office of Weights and Measures, and helped in shaping the legislation in regard to the legalization of the metric system in this country. The metric standards for the States of the Union were prepared under his supervision. It was therefore fitting that he should be appointed one of the scientific delegates to represent this government in Paris at an international conference having for its object the construction of a new meter as an international standard of length. In 1872 he attended the conference and actively participated in its deliberations, and when it had been decided to establish an International Bureau of Weights and Measures at Paris, its directorship was offered to him, but declined. While in Europe on the mission just referred to, he made a determination of Transatlantic longitudes, including in his operations Paris and Greenwich. It is rather singular that the first successful telegraphic longitude determination between these great observatories should have been made by an American, and his success in this undertaking was always looked upon by him as also a diplomatic triumph.

Hilgard was a charter member of the National Academy of Sciences, and took an active part in many of the investigations made by the Academy for the government. He conducted a magnetic survey of the country, under the auspices of the Academy, with means supplied out of the Bache Fund. In 1874 he was elected President of the American Association for the Advancement of Science.

His life was in many respects burdened by misfortune; for of his four children three died young and only one lived to man's estate and then died, leaving him childless and overwhelmed by grief at a time when a fatal disease had already begun its inroads on his mental and physical strength. This disease had already seriously impaired his health when he was appointed to the superintendency in 1881, which, to use his own words, came "too late."

There can be no doubt that he was conscious of his failing strength and ability while still occupying the position of Superintendent, for on more than one occasion he gave expression to the wish that the burden of his duties might be shifted to other shoulders.

His retirement took place in 1885, and from that time on his lingering illness entailed great sufferings, and several times brought him to the point of death. From each of these attacks he rallied with less power of resistance, until death relieved him of his sufferings, on May 8, 1891.

CHRISTIAN HEINRICH FRIEDRICH PETERS.

Christian Heinrich Friedrich Peters was born on September 19, 1813, at Coldenbüttel, in the Duchy of Schleswig. He studied mathematics and astronomy at Berlin between 1832 and 1836, and, after attaining the degree of Doctor of Philosophy, continued his education under the celebrated Gauss at Göttingen. In 1838 he was engaged to assist in a scientific expedition to Sicily for investigations on Mount Etna, and was employed, after the conclusion of this work, to direct the trigonometrical survey undertaken by the Neapolitan government.

Upon the outbreak of the revolutionary movements of 1848, it became impossible for him to retain his situation without suppressing his own sentiments in favor of freedom. Unable to conceal his liberal sympathies, he was dismissed and banished. But he soon returned to take an active part in the Sicilian insurrection, during which he served under Mieroslawski, first as captain and then as major of engineers. The suppression of the insurrection left him in imminent peril of capture by the Royalists ; but he finally effected his escape to France. He next went to Turkey, in hopes of obtaining scientific employment in that country; but the outbreak of the Crimean war put an end to these expectations, and he came to the United States in 1854. Here he found employment in the Coast Survey, and subsequently, in 1858, was appointed Professor of Astronomy at Hamilton College, Clinton, New York, and Director of the Observatory connected with that institution. He retained this position until his sudden death, in 1890. On the morning of July 19 in that year, his body was found on the steps leading to the building where he had lived, and it appeared that he had died on his way home from his customary work in the Observatory.

Notwithstanding his duties as a teacher, he found time during his life at Clinton for a great amount of astronomical observation. His principal work was that of determining the places of faint stars, with a view to the preparation of an extensive series of charts, part of which he published at his own expense in 1882. In the course of these observations he discovered many new variable stars and forty-eight new asteroids. He also made a long series of observations of solar spots. In 1874 he was chief of the expedition sent by the United States government to observe the transit of Venus. In 1876 he was chosen a member of the National Academy of Sciences.

His studies of the ancient catalogues of stars, such as that of Ptolemy, were extensive and profound, and part of his published work relates to these and similar subjects. His frequent journeys to Europe maintained his acquaintance with his professional colleagues of Germany and other countries, among whom he was always cordially welcomed. While the combative temperament which had formerly made him a soldier in the cause of Sicilian independence occasionally led him into controversies with regard to the extent of his personal rights, he made many friends, by whom he was greatly beloved.

FOREIGN HONORARY MEMBERS.

CHARLES JOHN MAXIMOWICZ.

Russia has been fruitful during the last seventy years in botanists of more than ordinary ability, as is shown by the mention from among them of such names as Besser, Bongard, Bunge and the Fischers, Herder, Ledebour, Maximowicz, Meyer and Regel, Ruprecht, Trautvetter, and Trinius, all well known to the botanical world. Of these this Academy has numbered among its Foreign Honorary Members only the subject of the present notice, C. J. Maximowicz, who was elected on October 10, 1888, and died on the 16th of February last.

Maximowicz was born on November 23, 1827, in the town of Toula in Central Russia, though most of his boyhood was spent in St. Petersburg. In 1844 he entered the University at Dorpat, where Dr. Bunge was then Professor of Botany, and upon graduation he received the appointment of Director's Assistant at the Dorpat Botanic Garden, whence he was removed in 1852 to the curatorship of the Imperial Botanic Garden in St. Petersburg. The next year he was commissioned as botanist and collector for the Garden to accompany the frigate Diana upon an expedition around the world, but the voyage was interrupted by the breaking out of the war with France and England, and Maximowicz left the ship upon reaching the Russian colony that had been recently established near the mouth of the Amur on the coast of Mandshuria. He here devoted himself to a botanical exploration of the then little known region bordering the Amur River, which he carried on assiduously under many difficulties for over two years, returning to St. Petersburg through Siberia in 1857. The critical study of his collections, and of such other material as had been received from the same territory, occupied him for two years longer, the results being embodied in his *Primitiæ Floræ Amurensis*. In this elaborate work he gave not only a detailed account of the plants, but a general view of the physical and botanical features of the country, the distribution of trees, and a comparison of the flora with others most nearly related to it. In acknowledgment of its scientific merits, he was awarded the Demidoff prize of five thousand roubles banco. He was now again sent to Eastern Asia to continue his botanical researches, and for four years travelled through Mandshuria, reaching the frontiers of Korea, and through the Japanese islands of Jesso, Nipon, and Kiusiu, returning to Europe in 1864.

From this time till the end of his life his main purpose was the preparation of a Flora of Japan and Eastern Asia. As Chief Botanist and Curator of the Herbarium at the Imperial Botanic Garden, and, after the death of Ruprecht, as Director of the Museum and Herbarium of the Imperial Academy of Sciences, he was burdened with official duties which continually interrupted and delayed the carrying out of this design, but it was never given up. Many contributions were published, chiefly in the Memoirs and Bulletins of the Imperial Academy, which were more or less directly related to this work, and which are often of interest to American botanists on account of the close relationship of the East Asiatic and the North American floras, and the consequent necessity of his taking into consideration American as well as Asiatic forms. Among these contributions may be noted revisions of the Asiatic *Rhamneæ* (1866), *Hydrangeæ* (1867), and *Rhododendreæ*

(1870), of the genus *Lespedeza* (1873), of the *Spiræaceæ* (1879), and of *Coriaria, Ilex, etc.* (1881); also a series of twenty papers entitled *Diagnoses Plantarum Novarum Japoniæ et Mandshuriæ* (1866–1876), and another series entitled *Diagnoses Plantarum Novarum Asiaticarum* (1877–1890). In 1873 he visited Finland and Sweden, especially to consult the herbarium of Thunberg at Upsal, and most of the summer of 1875 was spent in a visit to Scotland, Kew, Paris, and Germany. At about this time he was also expending much critical labor upon Japanese plants in aid of Franchet and Savatier in the preparation of their *Enumeratio Plantarum Japonicarum*, which owes its value very largely to this co-operation.

The last ten years of his life were occupied chiefly in the study of large and important collections from the previously almost inaccessible regions of Central Asia, especially those of Przewalski and Potanin from Tangout (Northern Tibet) and Mongolia, and in the elaboration of an extended report which was to be illustrated with a hundred or more finely engraved plates. Much of this was completed and ready for the press, but only the first parts are as yet published. The general results, as showing the characteristics of the flora of the region, were ably summarized by him in a paper read before the Botanical and Horticultural Congress held at St. Petersburg in 1884. To the great loss of botanical science he was cut off most unexpectedly in the midst of his labors, dying on February 16, 1891, of an attack of influenza, after a short illness.

The work of Maximowicz, as a botanist, is remarkable throughout for its extreme thoroughness and most scrupulous exactness in all its details, for good judgment and a purely scientific spirit, and he must always rank as a high authority in the department to which he devoted himself. As a man he was most estimable, of noble and spotless character, a scholar of high culture, and a most courteous and genial correspondent.

KARL WILHELM VON NAEGELI.

KARL WILHELM VON NAEGELI was born on March 27, 1817, at Kilchberg, near Zurich, and died at Munich, May 10, 1891. His education, begun in a private school at Zurich, was continued in the Gymnasium of that city until he entered the University of Zurich, where he received his doctor's degree in 1840. He had at first intended to study medicine, but his taste for natural science was so decided that he was allowed to go to Geneva, where he studied with De Candolle for a time. He afterwards went to Berlin, where his attention was turned to philosophical studies. He then proceeded to Jena, where he was associated with Schleiden, whose influence is clearly seen in the earlier writings of Naegeli. He was married in 1845, and soon after returned to Zurich, where he became Privatdocent, and afterwards Professor Extraordinarius. In 1852, Naegeli, after having declined a call to Giessen, was appointed Professor at Freiburg, in Breisgau. In 1855 he again returned to Zurich, where he was made Professor of General Botany in the new Polytechnic School. He resigned this position in 1857, and accepted an appointment as Professor of Botany and Director of the Botanic Garden at Munich, where he remained until his death. For the last twenty years of his life Naegeli's health was feeble, but he was nevertheless able to continue his scientific work during most of that period. In his feeble condition he was unable to rally from an attack of the influenza during the epidemic of 1889–90, and gradually succumbed to the disease.

During his long and active scientific career, Naegeli's influence was seen mainly in his writings, for, as a university lecturer, he did not succeed to the same extent as some of his contemporaries in attracting numbers of enthusiastic followers. Owing to certain peculiarities of temperament he was not personally popular with the botanists of Germany, and few of the younger botanists sought his instruction. That he was, however, capable of stimulating others to work of the highest grade is evident, if we consider that C. Cramer and Schwendener were his pupils and associates.

As a writer and investigator probably no botanist of the present century has had greater influence in shaping the course of modern botany than Naegeli. His botanical career began at a time when the influence of Schleiden was predominant, and naturally the early work of Naegeli bore the mark of Schleiden's peculiar views. But Naegeli was a man of decided originality, and united great accuracy as an observer with a genius for speculation and philosophical inquiry, and he soon freed himself from the limitations of Schleidenian conceptions. If, at the present day, we are obliged to admit that some of Naegeli's own theories have not stood the test of time, we must also admit that they were very suggestive and fruitful of results in their day, while, as an observer of facts, we can only admire his uniform accuracy and truthfulness. It is only natural that the theoretical views of Naegeli, formulated at a time when botanists were comparatively few and accurate observations scanty, should, in the light of accumulated modern observations, be superseded by other more tenable theories; but we must still continue to acknowledge that we are indebted to Naegeli for the solid foundation of more than one of the branches of botany which are now regarded as among the most interesting and important fields of modern research.

Naegeli was neither a pure systematist, nor strictly a physiologist in the modern sense. If he pursued systematic studies to some extent, it was with the view of preparing himself to discuss the abstract questions of the nature of species and the theory of descent. His detailed work on the genera *Cirsium* and *Hieracium* was undertaken with very much the same purpose as that of Darwin in his work on Cirrhipeds; namely, by mastering the specific differences to be found in a few large and variable genera, to prepare himself for the intelligent discussion of the relations and probable origin of species in general. Beyond this he felt little interest in systematic work. So far as his work on the nature of cell structure, the formation of the cell wall, the method of reproduction in Cryptogams, and the phenomena of fermentation is concerned, it was certainly physiological rather than systematic; but, using the terminology of the present day, it may be said that Naegeli was pre-eminently an histologist, and that the greater part of his theories and general views, so far as they were derived from his own work, had a histological basis. Unlike De Bary, Pringsheim, and the younger generation of German botanists, he did not attempt, to any extent, to study what may be called the life-history of any special group by means of cultures.

The histological work of Naegeli was admirable, and he was practically the first to introduce histological methods into the study of algæ and other groups. In his "Die neueren Algensysteme und Versuch zur Begründung eines eigenen Systems der Algen und Florideen" (1847) he accumulated a large mass of facts, and was the first to give an accurate account of the thallus of different species, and to show the necessity for studying the apical growth as a means of classification in this group. In his attempt to form a new system of classification he was less successful. He excluded the *Florideæ* from algæ; but although he was accurate as far as concerned the microscopic structure which he studied, he failed to recognize the true sexual relations of the *Florideæ*. In his paper "Beiträge zur Morphologie und Systematik der Ceramiaceæ"

(1861) his accuracy as an observer is shown, for in this paper he first figured correctly the young female condition of the *Florideæ*, but again failed to comprehend the true significance of his observation, and it was left to Bornet and Thuret, in 1867, to give the proper explanation and fix the true position of the *Florideæ*. It may be said that had Naegeli studied living instead of alcoholic material, he might perhaps have avoided his error. Naegeli's paper on the cell division in *Delesseria Hypoglossum* and on the structure of *Caulerpa prolifera* were also valuable contributions to our knowledge of algæ, and his "Gattungen einzelliger Algen" (1849), more purely systematic than his other works on algæ, still remains a classic monograph on the subject.

In his first histological paper (1841) on the development of pollen, and in later papers on the development of stomata and the structure of the root-apex, Naegeli proved himself to be a better observer than his teacher, Schleiden, and in two important papers published in 1844 and 1846 on nuclei and the formation and growth of vegetable cells, he showed emphatically that cell division is the true mode of vegetative cell formation. Although in his earlier paper on the growth of the leaf, Naegeli had been led to erroneous views on the nature of stems and leaves, nothing but praise can be said of his paper on the "Growth of the Stem and Root in Vascular Plants and the Arrangement of the Vascular Bundles" (1858). This paper is regarded by botanists as his most important histological work, and is the basis of the countless works of more recent writers on the subject. The enormous work of over six hundred pages on starch grains (1858) is full of important observations, and served as the foundation of the micellar theory, which has been alternately attacked and defended up to the present time, one phase of the discussion being the method of formation of cell walls by intussusception as opposed to apposition. For some time the preponderance of opinion rather favored Naegeli's theory of intussusception, but, although the question cannot as yet be said to be settled fully, the advocates of the theory of apposition have of late appeared to have the strongest evidence on their side, and physicists, as a rule, do not regard the micellar theory with much favor.

Naegeli's writings on fermentation, "Theorie der Gährung" (1879), with which may be classed properly his "Die niederen Pilze" (1877), represent rather his theoretical views based on the work of others than conclusions founded on his own work.

Although interesting and suggestive, they hardly possess the same weight as his other writings. He differs with many recent writers in believing that, among forms like bacteria, it is doubtful whether definite species exist, morphologically speaking, as in higher plants. It is still too soon to say whether his view on this point is correct or not; for, although most bacteriologists do not now agree with Naegeli, it must be admitted that the question is still an open one, and it would be rash to predict what would be the general verdict on this point a decade hence.

Up to this point we have spoken only of the special work which entitles Naegeli to be regarded as one of the foremost botanists of his time, unsurpassed and perhaps unequalled in his own special field. But his influence was felt beyond purely botanical circles, and he acquired by his writings on evolution a wide-spread reputation among all scientific men. In his doctor's thesis (1840) on the Swiss species of *Cirsium*, Naegeli foreshadowed a line of study which he afterwards worked out more elaborately in his later work on *Hieracium*, in which he made a minute and critical study of the variable species of a large genus serve as a groundwork for a consideration of the theory of descent. Early in life he believed in the absolute difference of species, although he urged the necessity of the study of development as that which gives real value to the knowledge of mature forms. In a later work, however, he stated that this early belief in the absolute difference of species "did not prevent his believing even then in the origin of species by descent." In his important paper, "Die Entstehung und Begriff der naturhistorischen Art" (1865), he discussed the Darwinian view of the origin of species, and stated that his own belief in the origin of species by descent had been definitely expressed in a paper published in 1856. He differed with Darwin in believing that variation occurred in a definite direction, — a view similar to that held by Gray, — and he was unable to accept natural selection as a sufficient explantion of evolution. His views were peculiar in that he believed that the different groups of plants originated independently from what he called "Urzellen," and, taking the different groups as they now exist, he failed to recognize a gradual development of the higher forms from the lower. Without stopping to consider his papers on the influence of external conditions in the formation of varieties and the theory of hybrid formation, we need here only refer to "Die mechanisch-physiologische Theorie der Abstammungslehre" (1884), a work in which he states the conclusions reached as the result of an unusually long and profound study. This work must be regarded as Naegeli's greatest contribution to speculative science, worthy to be classed with the masterpieces of the great writers on evolution. He maintains that variation arises from internal, not external causes, and that the transmission of hereditary characters depends not on the general protoplasm, but on a limited and definite part of it, the idioplasm. The enunciation of the general principle in the Abstammungslehre is forcibly and even brilliantly stated, and Naegeli's presentation of the subject has exerted and will continue to exert a marked influence on modern thought, although in some details he allows himself to indulge in views which are too purely speculative, and not borne out by the more exact microscopic work of a younger generation of workers.*

EDUARD SCHÖNFELD.

Eduard Schönfeld was born on December 22, 1828, at Hildburghausen, Germany. The comprehensive activity of his mind was early displayed in the course of his education, for he studied architecture and chemistry before finally selecting astronomy as his special field of work. His astronomical studies were begun at the University of Marburg, and continued, in 1852 and later, at Bonn, under the guidance of the illustrious Argelander. He took his degree in 1854, but had already in the previous year been appointed Assistant in the Observatory.

At this time, Argelander was entering upon the execution of his plan for the formation of a catalogue which should exhibit the approximate positions, and also the magnitudes, of all stars in the northern hemisphere not fainter than the ninth magnitude. He had made some preliminary observations for this purpose in 1852, but the work was definitely begun only after he had been joined by Schönfeld, who took a prominent part both in the observations themselves and in their reduction. The catalogue itself, which comprises 324,198 stars, was mainly drawn up by him.

In 1859, Schönfeld was appointed Director of the Observatory at Mannheim. Here he undertook the systematic observation of variable stars, and his two successive catalogues of these objects

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* A detailed account of Naegeli's life and work is to be found in the "Neue Zürcher Zeitung" for May 16, 1891, and in "Nature" for October 15, 1891.

are well known and highly valued among astronomers. With the Mannheim telescope he observed many nebulæ, and published a catalogue of these also.

Upon the death of Argelander, in 1875, Schönfeld was recalled to Bonn to succeed him. He then undertook the extension of the great catalogue above mentioned into the southern hemisphere, as far as the twenty-third degree of south declination. The number of stars thus added to the catalogue was 133,659. This additional catalogue, as well as that previously prepared under Argelander's direction, is accompanied by an atlas, showing the places of all the stars observed. The value of the entire work to astronomers can hardly be described in terms which would not seem extravagant to readers of other professions.

But the mere enumeration of the official occupations which formed the regular business of Schönfeld's life would give a very imperfect idea of his claim to the esteem and gratitude of his colleagues and contemporaries. As has already been suggested, his mind was distinguished by its breadth and versatility. An astonishing memory, very extensive reading, and pre-eminent ability in teaching and in writing, combined with a perfectly unpretentious and amiable disposition, made him, as may easily be imagined, a leader in his profession, commanding the admiration and good will of all who knew him personally or only by his publications. He was one of the most active and valuable members of the Astronomische Gesellschaft, and, as one of its secretaries in 1875 and later, was largely concerned in the publication of its journal, the "Vierteljahrsschrift," to which he frequently contributed articles of more than ordinary interest.

He died on May 1, 1891, after a prolonged illness, which, in the opinion of some of his friends, was to be ascribed to the unremitting labor to which he subjected himself in the observations for the extension of his great catalogue of stars, after his return to Bonn. His interest in astronomy continued unabated to the last, and the number of the "Astronomische Nachrichten" subsequent to that in which his death is announced contains a final article from his pen on a point in the history of astronomy, in explaining which his learning and ingenuity are, as usual, made evident.

The Academy has received an accession of eight members, — five Fellows, one Associate Fellow, and two Foreign Honorary Members.

Two Resident Fellows have resigned.

The roll of the Academy corrected to date includes the names of 186 Fellows, 89 Associate Fellows, and 69 Foreign Honorary Members.

MAY 26, 1891.

LIST

OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to January 1, 1892.)

RESIDENT FELLOWS. — 186.

(Number limited to two hundred.)

Class I. — *Mathematical and Physical Sciences.* — 78.

Section I. — 7.

Mathematics.

Gustavus Hay,	Boston.
Benjamin O. Peirce,	Cambridge.
James M. Peirce,	Cambridge.
John D. Runkle,	Brookline.
T. H. Safford,	Williamstown.
William E. Story,	Worcester.
Henry Taber,	Worcester.

Section II. — 10.

Practical Astronomy and Geodesy.

Seth C. Chandler,	Cambridge.
Alvan G. Clark,	Cambridgeport.
George B. Clark,	Cambridgeport.
J. Rayner Edmands,	Cambridge.
Henry Mitchell,	Boston.
Edward C. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
O. C. Wendell,	Cambridge.

Section III. — 46.

Physics and Chemistry.

A. Graham Bell,	Washington.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Arthur M. Comey,	Somerville
Josiah P. Cooke,	Cambridge.
James M. Crafts,	Boston.
Charles R. Cross,	Boston.
Amos E. Dolbear,	Somerville.
Thos. M. Drown,	Boston.
Charles W. Eliot,	Cambridge.
Moses G. Farmer,	Eliot, Me.
Thomas Gaffield,	Boston.
Wolcott Gibbs,	Newport, R. I.
Edwin H. Hall,	Cambridge.
Henry B. Hill,	Boston.
N. D. C. Hodges,	New York.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
Eben N. Horsford,	Cambridge.
Henry M. Howe,	Boston.
T. Sterry Hunt,	New York.
Charles L. Jackson,	Cambridge.
William W. Jacques,	Newton.
Alonzo S. Kimball,	Worcester.
Leonard P. Kinnicutt,	Worcester.
William R. Livermore,	Newport, R.I.
Joseph Lovering,	Cambridge.
Charles F. Mabery,	Cleveland.
Arthur Michael,	Worcester.
A. A. Michelson,	Worcester.
Charles E. Munroe,	Newport, R.I.
John U. Nef,	Worcester.
Lewis M. Norton,	Newton.
Robert H. Richards,	Boston.
Theodore W. Richards,	Cambridge.
Edward S. Ritchie,	Brookline.
A. Lawrence Rotch,	Boston.
Charles R. Sanger,	Cambridge.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Elihu Thomson,	Lynn.
John Trowbridge,	Cambridge.
Harold Whiting,	Cambridge.
Charles H. Wing,	Boston.
Edward S. Wood,	Cambridge.

Section IV. — 15.

Technology and Engineering.

John M. Batchelder,	Cambridge.
Winfield S. Chaplin,	St. Louis.
Eliot C. Clarke,	Boston.
James B. Francis,	Lowell.
Gaetano Lanza,	Boston.
E. D. Leavitt,	Cambridgeport.
William R. Lee,	Roxbury.
Hiram F. Mills,	Lawrence.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Boston.
Peter Schwamb,	Arlington.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

Class II. — *Natural and Physiological Sciences.* — 55.

Section I. — 9.

Geology, Mineralogy, and Physics of the Globe.

Thomas T. Bouvé,	Boston.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
O. W. Huntington,	Cambridge.
Jules Marcou,	Cambridge.
William H. Niles,	Cambridge.
Nathaniel S. Shaler,	Cambridge.
Warren Upham,	Somerville.

Section II. — 6.

Botany.

William G. Farlow,	Cambridge.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
Charles S. Sargent,	Brookline.
Charles J. Sprague,	Boston.
Sereno Watson,	Cambridge.

Section III. — 20.

Zoölogy and Physiology.

Alex. E. R. Agassiz,	Cambridge.
Robert Amory,	Boston.
James M. Barnard,	Milton.
Henry P. Bowditch,	Boston.
Wm. Brewster,	Cambridge.
Louis Cabot,	Brookline.
Harold C. Ernst,	Boston.
J. Walter Fewkes,	Boston.
Edw. G. Gardiner,	Boston.
Samuel Henshaw,	Cambridge.
Alpheus Hyatt,	Cambridge.
Theodore Lyman,	Brookline.
Edward L. Mark,	Cambridge.
Charles S. Minot,	Boston.
Edward S. Morse,	Salem.
James J. Putnam,	Boston.
Samuel H. Scudder,	Cambridge.
William T. Sedgwick,	Boston.
Henry Wheatland,	Salem.
James C. White,	Boston.

Section IV. — 20.

Medicine and Surgery.

Samuel L. Abbot,	Boston.
Henry I. Bowditch,	Boston.
Edward H. Bradford,	Boston.
Arthur T. Cabot,	Boston.
David W. Cheever,	Boston.
Benjamin E. Cotting,	Roxbury.
Frank W. Draper,	Boston.
Thomas Dwight,	Boston.
Reginald H. Fitz,	Boston.
Charles F. Folsom,	Boston.
Richard M. Hodges,	Boston.
Oliver W. Holmes,	Boston.

Frederick I. Knight,	Boston.
Francis Minot,	Boston.
Samuel J. Mixter,	Boston.
Wm. L. Richardson,	Boston.

George C. Shattuck,	Boston.
Henry P. Walcott,	Cambridge.
John C. Warren,	Boston.
Henry W. Williams,	Boston.

Class III. — *Moral and Political Sciences.* — 53.

Section I. — 10.

Philosophy and Jurisprudence.

James B. Ames,	Cambridge.
Phillips Brooks,	Boston.
Charles C. Everett,	Cambridge.
Horace Gray,	Boston.
John C. Gray,	Boston.
Nathaniel Holmes,	Cambridge.
John Lowell,	Newton.
Henry W. Paine,	Cambridge.
Josiah Royce,	Cambridge.
James B. Thayer,	Cambridge.

Section II. — 17.

Philology and Archæology.

William S. Appleton,	Boston.
Lucien Carr,	Cambridge.
Franklin Carter,	Williamstown.
Joseph T. Clarke,	Boston.
Henry G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Henry W. Haynes,	Boston.
Bennett H. Nash,	Boston.
Frederick W. Putnam,	Cambridge.
F. B. Stephenson,	Boston.
Joseph H. Thayer,	Cambridge.
Crawford H. Toy,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
Edward J. Young,	Waltham.

Section III. — 17.

Political Economy and History.

Charles F. Adams,	Quincy.
Edward Atkinson,	Boston.
John Cummings,	Woburn.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
A. C. Goodell, Jr.,	Salem.
Henry C. Lodge,	Boston.
Augustus Lowell,	Boston.
Edward J. Lowell,	Boston.
Francis Parkman,	Boston.
Andrew P. Peabody,	Cambridge.
John C. Ropes,	Boston.
Denman W. Ross,	Cambridge.
F. W. Taussig,	Cambridge.
Henry W. Torrey,	Cambridge.
Francis A. Walker,	Boston.
Robert C. Winthrop,	Boston.

Section IV. — 9.

Literature and the Fine Arts.

George S. Boutwell,	Groton.
Martin Brimmer,	Boston.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
Charles G. Loring,	Boston.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.
John G. Whittier,	Amesbury.

ASSOCIATE FELLOWS. — 89.

(Number limited to one hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 33.

SECTION I. — 4.

Mathematics.

Simon Newcomb,	Washington.
H. A. Newton,	New Haven.
James E. Oliver,	Ithaca, N.Y.
J. N. Stockwell,	Cleveland, Ohio.

SECTION II. — 12.

Practical Astronomy and Geodesy.

W. H. C. Bartlett,	Yonkers, N.Y.
S. W. Burnham,	San José, Cal.
Geo. Davidson,	San Francisco.
Wm. H. Emory,	Washington.
Asaph Hall,	Washington.
George W. Hill,	Washington.
E. S. Holden,	San José, Cal.
Sam. P. Langley,	Washington.
T. C. Mendenhall,	Washington.
William A. Rogers,	Waterville, Me.
George M. Searle,	New York.
Chas. A. Young,	Princeton, N.J.

SECTION III. — 11.

Physics and Chemistry.

Carl Barus,	Washington.
J. Willard Gibbs,	New Haven.
Frank A. Gooch,	New Haven.
S. W. Johnson,	New Haven.
M. C. Lea,	Philadelphia.
J. W. Mallet,	Charlottesville, Va.
A. M. Mayer,	Hoboken, N. J.
Ira Remsen,	Baltimore.
Ogden N. Rood,	New York.
H. A. Rowland,	Baltimore.
L. M. Rutherfurd,	New York.

SECTION IV. — 6.

Technology and Engineering.

Henry L. Abbot,	New York.
Geo. W. Cullum,	New York.
Geo. S. Morison,	New York.
John Newton,	New York.
William Sellers,	Philadelphia.
W. P. Trowbridge,	New Haven.

CLASS II. — *Natural and Physiological Sciences.* — 28.

SECTION I. — 14.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
James D. Dana,	New Haven.
Sir J. W. Dawson,	Montreal.
F. A. Genth,	Philadelphia.
James Hall,	Albany, N.Y.
F. S. Holmes,	Charleston, S.C.
Clarence King,	New York.
Joseph Le Conte,	Berkeley, Cal.
J. Peter Lesley,	Philadelphia.
J. S. Newberry,	New York.
J. W. Powell,	Washington.
R. Pumpelly,	Newport, R.I.
Geo. C. Swallow,	Columbia, Mo.

Section II. — 2.

Botany.

A. W. Chapman,	Apalachicola, Fla.
D. C. Eaton,	New Haven.

Section III. — 7.

Zoölogy and Physiology.

Joel A. Allen,	New York.
G. B. Goode,	Washington.
O. C. Marsh,	New Haven.
H. N. Martin,	Baltimore.
S. Weir Mitchell,	Philadelphia.
A. S. Packard,	Providence.
A. E. Verrill,	New Haven.

Section IV. — 5.

Medicine and Surgery.

John S. Billings,	Washington.
Jacob M. Da Costa,	Philadelphia.
W. A. Hammond,	New York.
Alfred Stillé,	Philadelphia.
H. C. Wood,	Philadelphia.

Class III. — *Moral and Political Sciences.* — 28.

Section I. — 8.

Philosophy and Jurisprudence.

T. M. Cooley,	Ann Arbor, Mich.
D. R. Goodwin,	Philadelphia.
A. G. Haygood,	Oxford, Ga.
James McCosh,	Princeton, N.J.
Charles S. Peirce,	New York.
Noah Porter,	New Haven.
E. G. Robinson,	Providence.
Jeremiah Smith,	Dover, N.H.

Section II. — 7.

Philology and Archæology.

A. N. Arnold,	Pawtuxet, R.I.
Timothy Dwight,	New Haven.
D. C. Gilman,	Baltimore.
A. C. Kendrick,	Rochester, N.Y.
E. E. Salisbury,	New Haven.
A. D. White,	Ithaca, N.Y.
W. D. Whitney,	New Haven.

Section III. — 7.

Political Economy and History.

Henry Adams,	Washington.
Geo. P. Fisher,	New Haven.
M. F. Force,	Cincinnati.
Henry C. Lea,	Philadelphia.
Edward J. Phelps,	Burlington, Vt.
W. G. Sumner,	New Haven.
J. H. Trumbull,	Hartford.

Section IV. — 6.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich.
L. P. di Cesnola,	New York.
F. E. Church,	New York.
R. S. Greenough,	Florence.
William W. Story,	Rome.
Wm. R. Ware,	New York.

FOREIGN HONORARY MEMBERS.—69.

(Elected as vacancies occur.)

Class I.—*Mathematical and Physical Sciences.*—24.

Section I.—6.

Mathematics.

John C. Adams,	Cambridge.
Sir George B. Airy,	London.
Francesco Brioschi,	Milan.
Arthur Cayley,	Cambridge.
Charles Hermite,	Paris.
J. J. Sylvester,	Oxford.

Section II.—4.

Practical Astronomy and Geodesy.

Arthur Auwers,	Berlin.
J. H. W. Döllen,	Pulkowa.
H. A. E. A. Faye,	Paris.
Otto Struve,	Pulkowa.

Section III.—11.

Physics and Chemistry.

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
R. Bunsen,	Heidelberg.
H. L. F. Helmholtz,	Berlin.
A. W. Hofmann,	Berlin.
Mendeleeff,	St. Petersburg.
Marignac,	Geneva.
Lord Rayleigh,	Witham.
Sir H. E. Roscoe,	London.
Sir G. G. Stokes,	Cambridge.
Julius Thomsen,	Copenhagen.

Section IV.—3.

Technology and Engineering.

Marquis de Caligny,	Versailles.
F. M. de Lesseps,	Paris.
Sir Wm. Thomson,	Glasgow.

Class II.—*Natural and Physiological Sciences.*—25.

Section I.—6.

Geology, Mineralogy, and Physics of the Globe.

H. Ernst Beyrich,	Berlin.
Alfred Des Cloizeaux,	Paris.
A. E. Nordenskiöld,	Stockholm.
C. F. Rammelsberg,	Berlin.
Sir A. C. Ramsay,	Beaumaris.
Heinrich Wild,	St. Petersburg.

Section II.—5.

Botany.

J. G. Agardh,	Lund.
Alphonse de Candolle,	Geneva.
Sir Joseph D. Hooker,	London.
Julius Sachs,	Würzburg.
Marquis de Saporta,	Aix.

SECTION III. — 10.

Zoölogy and Physiology.

P. J. Van Beneden,	Louvain.
Du Bois-Reymond,	Berlin.
Thomas H. Huxley,	London.
Albrecht Kölliker,	Würzburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
C. F. W. Ludwig,	Leipsic.
Sir Richard Owen,	London.
Louis Pasteur,	Paris.
J. J. S. Steenstrup,	Copenhagen.

SECTION IV. — 4.

Medicine and Surgery.

Sir Wm. Bowman,	London.
C. E. Brown-Séquard,	Paris.
Sir James Paget,	London.
Rudolph Virchow,	Berlin.

CLASS III. — *Moral and Political Sciences.* — 20.

SECTION I. — 3.

Philosophy and Jurisprudence.

James Martineau,	London.
Henry Sidgwick,	Cambridge.
Sir James F. Stephen,	London.

SECTION II. — 7.

Philology and Archæology.

John Evans,	Hemel Hempstead.
Pascual de Gayangos,	Madrid.
Benjamin Jowett,	Oxford.
J. W. A. Kirchhoff,	Berlin.
G. C. C. Maspero,	Paris ?
Max Müller,	Oxford.
Sir H. C. Rawlinson,	London.

SECTION III. — 6.

Political Economy and History.

Duc de Broglie,	Paris.
Ernst Curtius,	Berlin.
W. Ewart Gladstone,	Hawarden.
Charles Merivale,	Ely.
Theodor Mommsen,	Berlin.
Jules Simon,	Paris.

SECTION IV. — 4.

Literature and the Fine Arts.

Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Leslie Stephen,	London.
Lord Tennyson,	Isle of Wight.

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