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# ARTICLE I.

## DESCRIPTION OF A SKULL OF MEGALONYX LEIDYI, n.sp.

BY JOSUA LINDAHL, PH.D.,
SPRINGFIELD, ILL.

**Read before the American Philosophical Society, January 2, 1891.**

The specimen to be described on the following pages belongs to Bethany College, Lindsborg, Kansas. It was placed in my hands for description, three years ago, by Prof. J. A. Udden, at that time holding the chair of Natural History in Bethany College, and I wish herewith to express my obligation to the President of the said institution, the Rev. C. A. Svensson, for having allowed me to retain it so long, no less than to Prof. Udden, who first offered me this opportunity, and who, at my request, has communicated a geological sketch of the locality where it was discovered.

This is his letter:

DR. J. LINDAHL, Springfield, Ill.:

*Dear Sir:*—The fossil skull of Megalonyx, which I sent you three years ago, was found by a man in excavating a sand pit near the southwest corner of Harper township, in McPherson county, Kansas.

The watershed between the Kansas and the Arkansas systems runs through McPherson county from east to west. Near the centre of the county it crosses at right angles a shallow trough about ten miles wide, which contains a series of small, undrained basins, and is known by well diggers in the county as the "old river bed." This trough has formerly been one hundred and twenty five feet deeper than it now is, being filled to that extent by sediments burying the red shales into which it is cut. Taken in ascending order, these sediments consist of (1) gravel and sand, containing rolled boulders of clay and angular fragments of cretaceous shales of various sizes up to a weight of a ton and more (*from near the bottom of this gravel the skull was taken*); (2) a stratum of clay, observed only in two places, and not known to be continuous over any considerable area; (3) a stratum of volcanic dust several feet in thickness, seen at six different localities, extending twelve miles in a line across the trough; (4) a fine dull orange-colored loam, upwards of seventy-five feet in thickness, and occasionally resembling loess.

From the gravel and the sand have been taken the following fossils, determined by Profs. E. D. Cope and R. Ellsworth Call:

*Equus major* DeKay.
*Sphærium striatum* Lam.
*Sphærium sulcatum* Lam.
*Pisidium abditum* Haldeman.
*Anodonta*, sp.
*Valvata tricarinata* Say.
*Gammarus*, sp.

Beds like these are found at various places on the Western plains, but they have suffered greatly by erosion. Their occurrence in McPherson county is at a point marking the crossing of a line of minimum erosion (the watershed) over another line of maximum development (the trough).

A study of the region and the deposits, in my opinion, shows that (1) previous to the deposition of the Pleistocene, the country was traversed by drainage channels considerably deeper than at present; (2) the time of the making of the gravel and the sand was probably coincident with a period of increasing humidity; (3) the gravel and the volcanic dust were deposited in waters that did not cover the cretaceous ledges in the vicinity; (4) floating ice was present as an effective transporting agent, when the sand and gravel were being laid down.

In the gravel, a small boulder was found containing fossils, which have been identified by Mr. E. O. Ulrich as belonging to the Lower Carboniferous. Large boulders are common, consisting of a pure white aggregate of microscopic crystals of carbonate of lime. Specimens of this material have been examined by Mr. George P. Merrill, who says he has seen similar material from the Cretaceous of Texas. Both of these occurrences point to a southern extension of the water in which the deposits were made.

Yours, most sincerely, J. A. Udden.

Augustana College, Rock Island, Ill., Dec. 10, 1890.

The specimen has not the appearance of having been exposed to violence or to the vicissitudes of long transportation previous to its discovery, its present defects evidently being caused by careless handling afterwards. Prof. Udden had, therefore, good reasons for his hopes that the balance of the skeleton might be found in the same gravel pit. These hopes proved futile, notwithstanding his energetic labors, but he was rewarded by recovering the only missing portion of the right zygoma, and also a dorsal vertebra which may or may not have belonged to the same individual.

The original discoverers of the skull, ignorant of its value, removed both the canine molars, to keep them as curiosities, and, for the same purpose, broke off the protruding ends of five of the other molars, leaving only the 2d in the left maxilla and the 2d and 4th in the right. In this operation they also removed portions of the alveolar walls of the 1st and 5th molars and of the palatine and pterygoid bones (Pl. III). The left canine molar was afterwards returned, though short of its pulp end; also, the inner half of the piece removed from the 3d right molar. The descending ramus of the left zygoma as well as the intermaxillary bones were not found.

Prof. Joseph Leidy (in his *Memoir of the Extinct Sloth Tribe of North America*, Smithsonian Contributions to Knowledge, Dec., 1853) described two skulls of *Megalonyx jeffersoni* Harlan. One of them, originally belonging to Dr. D. D. Owen's collection, is now the property of the Indiana State University at Bloomington, Ind. I will here refer to that specimen as the *Owen specimen.* The other, discovered by Dr. M. W. Dickeson, belongs to the Philadelphia Academy of Sciences. I will call it the *Dickeson specimen.* These two skulls and the *Kansas specimen* now before me are, as far as known, the only *Megalonyx* skulls hitherto preserved in any collection. The Kansas specimen is specifically distinct from the other two, and has also in other respects a particular value, in so far as it shows the structure of the entire zygomatic arch and of the turbinals, which bones were nearly destroyed in the specimens described by Dr. Leidy. This paper will, therefore, supplement his as a memoir on the genus *Megalonyx.* For easier comparison with Dr. Leidy's figures, the figures illustrating this paper have been drawn, with few exceptions, to the same scale as his. They were executed by my old friend, Mr. A. M. Westergren, for twenty-five years the able artist in the Royal Swedish Academy of Science, in Stockholm, now with Prof. Alexander Agassiz, of Harvard.

Judging from the more perfect obliteration of the sutural connections in the Dickeson specimen, Dr. Leidy has demonstrated that it belonged to an older individual than the Owen specimen. The same argument places the age of the Kansas specimen between the other two. The sagittal and occipito-parietal sutures are less open than in the Owen specimen, but more so than in the Dickeson specimen. The temporo-parietal sutures are entirely obliterated, and so is the suture between the basi-occipital and the basi-sphenoidal bones, both of which sutures are distinct in the Owen specimen.

*Lateral view.*—The obvious difference in the sagittal contour in the three skulls (compare Pl. I with Leidy's Pl. I and Pl. IV) may be explained as owing to difference in age, and would then confirm the conclusion derived from comparing the sutural connections. The still more striking difference in the facial contour in the two specimens of *M. jeffersoni* is most likely a secondary sexual character. May it not be that the males of these animals, like those of the recent cystophorine seals, had some special adaptation of their nose for vocal purposes? The Kansas specimen agrees in this contour more closely with the Dickeson specimen than with the Owen specimen; the latter having the nasal vault raised higher than the cranial portion, which is not the case in the other two. It may thus be inferred that these two are females, the Owen specimen a male.

As stated above, but little remains of a *zygomatic arch* in the two specimens of *M. jeffersoni.* A special interest attaches to this arch on account of its extreme diversity of form in the different genera of Edentates. Reinhardt* inferred from the

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* Prof. J. Reinhardt: "Kæmpedovendyr-Slægten *Cœlodon;*" Copenhagen, 1878, pp. 325, 326.

strongly developed sagittal crest and temporal fossa that the zygomatic arch in *Megalonyx* may, not unlikely, prove to be completely closed. Our specimen shows that he was correct in his conclusion. I will here give a detailed description of this structure.

*The zygomatic arch.*—The zygomatic process of the squamosal bone projects outward and forward, as in *M. jeffersoni.* Its upper border descends first in a *concave* curve for about 8 cm. from the inion (thereby *differing from M. jeffersoni*, in which the corresponding line is *strongly convex*, Leidy, *l.c.*, Pl. I); along the following 4 cm. it deviates less from a horizontal direction; and, finally, in its last 4 cm., it rises gently upward to meet the border of the malar bone, about 15 cm. from its origo on the border of the inion.

The glenoid fossa is curved outward and forward, measuring 5 cm. in length and 2.5 cm. in greatest width. There is but a rudimentary postglenoidal process, but the antero-exterior margin of the fossa is expanded into a horizontally flattened exglenoidal process. The inferior border of the bone extends 4 cm. in advance of this process, and there meets the postero-inferior process of the malar bone. The space between these two processes is more or less roughened.

The external surface of the zygomatic process, viewed from above, is sigmoid; but between its upper and lower margins it is more or less concave throughout. Its least vertical diameter is 32 mm.

The anterior end of the zygomatic process slants upward and forward with a gentle curve and finally makes a sudden turn upward and backward. The corresponding emargination in the malar bone does not describe a similar curve, but passes, in its upper portion, with a beveled edge, behind (inside of) the edge of the zygomatic process. The sutures are entirely obliterated in the arch of the right side, but the left arch has been fractured accidentally, and the suture cracked open. However, even on the right side (Pl. I) the location of this suture may be seen as a line, from both sides of which the faces of the two bones slope in different directions.

There is a rough semicircular ridge on the inside of the zygomatic process, passing from its infero-anterior point to a point perpendicularly above the same. In front of this ridge is a broad shallow fossa extending over a considerable portion of the malar bone.

Leidy's description of the *malar process of the maxilla* in *M. jeffersoni* (*l.c.*, p. 9) applies also to *M. leidyi*, except in the latter having the infra-orbital canals double, a horizontal septum dividing each into two canals, one immediately above the other. This *individual* presents, also, an asymmetry in these canals, for, whilst that of the right side has but a rudimentary septum forming a complete partition only for a short distance, a little behind the middle of the canal, the septum in the canal of the left side is complete through its entire length, and is 6 mm. thick in the centre of its anterior border. The anterior orifices are vertically oval, that of the right side measuring 13.5 × 9 mm.; the upper orifice on the left side measuring 8 × 5 mm., and the lower, 11 × 9 mm.

Resting on the zygomatic process of the maxilla, the root of the *malar bone* projects outward, backward, and downward, its antero-posterior diameter being 12 mm., the intero-exterior 21.5 mm. in its narrowest place, about 12 mm. below the summit of the curve of the said process. About 9 mm. further down, on the interior side, is a tuberosity forming the superior termination of an area for muscular attachment. This area, 10 mm. wide and 41 mm. long, twists itself around the border of the bone, so that its lower end faces directly forward. It is divided by a low, median longitudinal ridge into two facets.

From the border, bearing this area, the external surface of the bone turns outward and backward, and at the same time expands both upward and downward; the anterior border of the upper expansion forms the exterior border of the orbit, and terminates about 5 cm. above the inferior orbital border in a postorbital protuberance; whilst the downward expansion is prolonged into a free *descending ramus*, terminating abruptly, 96 mm. below the inferior border of the orbit. A low ridge passes from the infero-posterior corner of this ramus, on its exterior face, diagonally upward and forward, dividing that face into two concave facets, of which the antero-inferior is triangular in form, the other somewhat rhomboidal. The inferior as well as the posterior borders of the ramus are attenuated to sharp edges; its anterior face is triangular, and by a sharp ridge set off from the exterior face; its interior face is smooth and convex.

Posterior to a line, which may be drawn from the postorbital protuberance of the malar bone to the posterior margin of the descending ramus, the exterior face of the bone bends more strongly backward, and the corresponding line on the interior face is the anterior margin of the broad shallow fossa which extends to the semicircular ridge near the distal end of the zygomatic process of the squamosal. The free postero-inferior margin of this laminar body forms a sharp edge, and, on the external face, bordering on this edge, is seen a semicordate muscular impression, pointed behind, oval in front, and reaching nearly half way towards the inferior margin of the orbit.

A line drawn from the postorbital protuberance of the malar to the nearest point of the zygomatic process of the squamosal, may be regarded as the base of the *ascending ramus* of the latter. Below this line the external face of the bone slopes downward and forward; above the same line the ascending process slopes upward and inward. It also points strongly backward. Its free borders are nearly straight, except near the apex, where they suddenly converge, and near their bases, where the anterior border gently curves convexly upon the postorbital protuberance, whilst the posterior border makes a concave curve towards the superior margin of the zygomatic process. The internal face of the ramus is strongly convex.

The entire span of the zygomatic arch is 25 cm., from inion to the farthest point on the anteorbital margin, and 11.8 cm. from the inner curve of the zygomatic process of the squamosal to the inner curve of the corresponding process of the maxilla. The distance between the apices of the two rami of the malar is 18.4 cm.

*Superior view.*—One of the most obvious differences in the three skulls is presented by the divergence of the temporal ridges. A comparison of Plate II with Leidy's Plate II will tell this at a glance. The angle between these ridges is acute in the Owen specimen, but broadly obtuse in the other. But the Dickeson specimen has the same angle still more obtuse, and no specific value can therefore be attached to these differences.

*Posterior view* (Pl. IV, Fig. 2).—Here the differences are more important. In *M. jeffersoni* (*l.c.*, Pl. VI, Fig. 3) the outline of the inion is semicircular; in *M. leidyi* it is decidedly polygonal, though with rounded corners. The upper portion of the inion is in *M. jeffersoni* flattened, and bordered below by a transverse crest. In *M. leidyi* the corresponding portion bulges out to form a broad tuberosity, bordered below by two transverse fossæ, one on each side of the vertical crest.

*Foramen magnum* is transversely oval, its horizontal and vertical diameters respectively 43 mm. and 34 mm. In *M. jeffersoni* this foramen is circular, its diameter 34 mm. ("16 lines," Leidy).

*Anterior view.*—In comparing Leidy's Pl. VI, Fig. 2, with our Pl. IV, Fig. 1, it should be remembered that the specimen figured by Leidy has the intermaxillaries preserved, which ours has not. Other differences are such that it is hard to tell what is of really specific importance or may be due to age or sex.

*The nasal cavity.*—The internal structure of the nose is much better preserved in our specimen than in either of the skulls described by Leidy. A brief description will therefore be in place here.

Behind the incisive foramen the anterior end of the hard palate is turned upward and slightly inclined backward between the alveolar walls of the canine molars, to a height of about 25 mm. Its upper edge is centrally produced in a triangular process with acuminate apex. A nasal crest of the maxillaries commencing about 65 mm. behind its anterior border, and resting on the median line of the floor of the cavity, abuts on the front wall just described and participates in forming the apex of its triangular process.

The upper bony septum of the cavity is formed by a perpendicular lamina, 48 mm. high and 2 to 4 mm. thick in its anterior margin. This lamina, which extends 115 mm. backward, has its free edge grooved for the attachment of the cartilaginous septum. The distance between the antero-inferior corner of this lamina and the apex of the triangular process below is 26 mm. The anterior margins of the nasal bones project about 25 mm. beyond the perpendicular lamina. Attached to the intero-inferior margins of the nasals, and about 30 mm. behind their anterior margins, appear the anterior margins of the *ethmo-turbinals* as vertical laminæ, until in the postero-superior recesses of the cavity, they expand their convoluted portions.

The *maxillo-turbinals* are very large. Their anterior extremities show them to be borne on the lateral walls of the cavity, near the proximal extremity of the canine molars, and thence to extend both upward and downward. The upper portion bends around the alveole and bulges out externally, following, with a small interspace, the form of the wall of the cavity. The lower portion extends into the cavity between the maxillary wall and the nasal crest. The inner side facing the narial septum is flattened. The vertical height of the whole maxillo-turbinal is at least 8 cm., the upper portion being the higher; the antero-posterior diameter is about 9 cm. At the anterior margin of its root on the maxillary wall is seen a circular foramen with raised borders, appearing as the projecting end of a tube.

Capacious air sinuses extend backward in the root of the pterygoid (Pl. III), and branch off from there forward into the alveolar wall of the maxilla.

*Inferior view, and sections of the skull.*—The distinctive characters of *M. leidyi* are best expressed in its proportions. Leaving out measurements and plates from Leidy's "Memoir," his description would exactly fit to our specimen, as well. Perhaps the most striking peculiarity of the latter is the far lesser prominence (depth) of its maxillary portion. This will be most readily appreciated by comparing the sections, Pl. V, Figs. 1–6, which were constructed with great care, Figs. 1, 3 and 5 from the Kansas specimen, and Figs. 2, 4 and 6 from a plaster cast of the Owen specimen.

Sections 1 and 2 were taken vertically and longitudinally through the sagittal crest. The vertical distance between the base of the cranium and the most projecting point of the hard palate in the specimens measured, is respectively 34 mm. and 60 mm.

Sections 3 and 4 are transverse, nearly vertical, sections of the same specimens, immediately in front of their 2d molars and anteorbital margins.

Sections 5 and 6 are also transverse and vertical, passing through the anterior borders of the *foramina rotunda* [the locations of these foramina are indicated by asterisks (**)], and thus at or near the narrowest portion of the cranium.

The pterygoid processes converge more rapidly forward in *M. jeffersoni* (*l.c.*, Pl. III) than in *M. leidyi* (Pl. III), their most approximated points in the former being just below the said foramina, but in the latter, at least 5 cm. more forward. Their roots bend more outwardly, their horizontal interior portions are narrower, and the anterior end of the basi-sphenoid, exposed to view between their inner margins, is broader in the line of the section in *M. jeffersoni* than in *M. leidyi*. The area between the root of the pterygoid process and the inferior border of the temporal fossa, in *M. jeffersoni*, overhangs the said process, sloping upward and outward about 30°, and extending as a plane in that direction about 3 cm., when it suddenly bends vertically upward, and finally makes a sudden turn inward and upward to its margin on the sagittal crest. The same surface in *M. leidyi* rises at once from *foramen rotundum* more than 60°, and curves gently up to the crest without any sudden bend. Sections 5 and 6 will show these differences plainly.

*Dentition.*—The left canine molar, as much as is left of it, as well as the alveoles of these molars, are but very slightly curved and are of uniform diameter. This species thus belongs to Group "B," in Cope's Synoptic Table (E. D. Cope: *Preliminary Report on the Vertebrata discovered in the Port Kennedy Bone Cave*, Am. Phil. Soc., Vol. xii, 1871, p. 85). The group comprises but two other known species, viz., *M. wheatleyi* Cope, and *M. dissimilis* Leidy. Cope makes the following distinction between the two:

"Molars triangular; canine molars less compressed—*M. wheatleyi.*"

"Last molar oval; canine molars more compressed—*M. dissimilis.*"

The third species of the group should be characterized thus:

Last molar ovato-triangular; the others quadrangular; canine molars less compressed—*M. leidyi.*

It might be added that the exterior dentine layer, in both of the former species, is thinnest at the bulge, whereas in *M. leidyi* it has its maximum thickness at the bulge.

The figures of the teeth (Pl. V, Figs. 7–9) are drawn with particular care. It should be remembered that the triturating surfaces are preserved only of the 1st and 2d molars in the left maxilla, and of the 2d, 3d (partly), and 4th in the right maxilla, and that the two 5th molars are broken off so high up as to expose their pulp cavities (compare Pl. III). Even regardless of this, the teeth are not perfectly symmetrical.

In naming this species for the venerable palæontologist, Prof. JOSEPH LEIDY, M.D., LL.D., of the University of Pennsylvania, I make but a small acknowledgment of his admirable work on the osteology of the fossil Edentates—one of the numerous fields in which his master mind has illuminated the way on which humbler servants of Science endeavor to follow his lead.

*Comparative Measurements of the Skulls of Megalonyx jeffersoni*[1] *and M. leidyi.*

| | *M. jeffersoni.* | | *M. leidyi.* |
|---|---|---|---|
| | *Owen Spec.* | *Dickeson Spec.* | *Kansas Spec.* |
| | *mm.* | *mm.* | *mm.* |
| Length of skull from occipital condyles to anterior margin of 1st molar alveoli | 356 | 336 | 343 |
| Length from inion to anterior margins of nasals | 311 | .... | 309 |
| Length of temporal fossa to postorbital protuberance | 197 | 197 | 199 |
| Depth of temporal fossa in a straight line | 102 | 114 | 108 |
| Length of face from postorbital protuberance | 119 | 112 | 115 |
| Height of face to middle of hard palate[2] | 153 | 146 | 136 |
| " " at anterior extremity | 127 | 127 | 101 [3] |
| Breadth " " " | 95 | 95 | 83 |
| " " at sides of 1st molar alveoli | 114 | 114 | 101 |
| " " at postorbital protuberances | 127 | 138 | 123 |
| Diameter of orifice of the nose | 89 | 89 | 77 |
| Breadth of intermaxillaries, across their centres | 85 * | .... | 45 [3] |
| Breadth of hard palate between 1st molars | 60 † | .... | 40 |
| Length of interval between 1st and 2d molars | 50 † | .... | 40 |
| Length of face from 1st to last molar alveolus | 178 | 171 | 150 |
| Length of maxilla from 2d to 5th molar alveoli, inclusive | 95 † | 95 * | 80 § |
| Breadth of cranium at narrowest part of the temporal region | 89 | 102 | 91 |
| Length of sagittal crest | 127 | 127 | 144 [4] |
| Height of inion from inferior margin of *foramen magnum* | 110 | 110 | 107 |
| Breadth of inion at mastoid processes | 159 | 165 | 165 |

Capacity of brain cavity, 448 cu. cm. This indicates the weight of the brain to have been 16 oz. (according to Owen's rule: *Comp. Anat. and Physiol. of Vertebrates,* Vol. iii, p. 144; the footnote).

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[1] According to Leidy (*l.c.* p. 13), unless otherwise stated. His measurements, in inches and lines, have here been reduced to millimetres.

[2] This measurement is taken in a vertical plane passing close in front of the anteorbital borders.

[3] Although the intermaxillary bones are missing, the areas of their attachment to the maxilla are well marked.

[4] The anterior terminus of this crest is determined somewhat arbitrarily, the parietal bones leaving a wide fissure between their margins, which gradually diverge and pass over into the ridges curving outward and forward to the postorbital protuberances.

* Measured on Leidy's plates.

† Measured on a plaster cast.

§ Estimated.

## EXPLANATION OF THE PLATES.

### *Plate I.*

Lateral view—two-thirds natural size.

### *Plate II.*

Superior view—two-thirds natural size.

### *Plate III.*

Inferior view—two-thirds natural size.

### *Plate IV.*

Fig. 1. Anterior view—two-thirds natural size.
Fig. 2. Posterior view—two-thirds natural size.

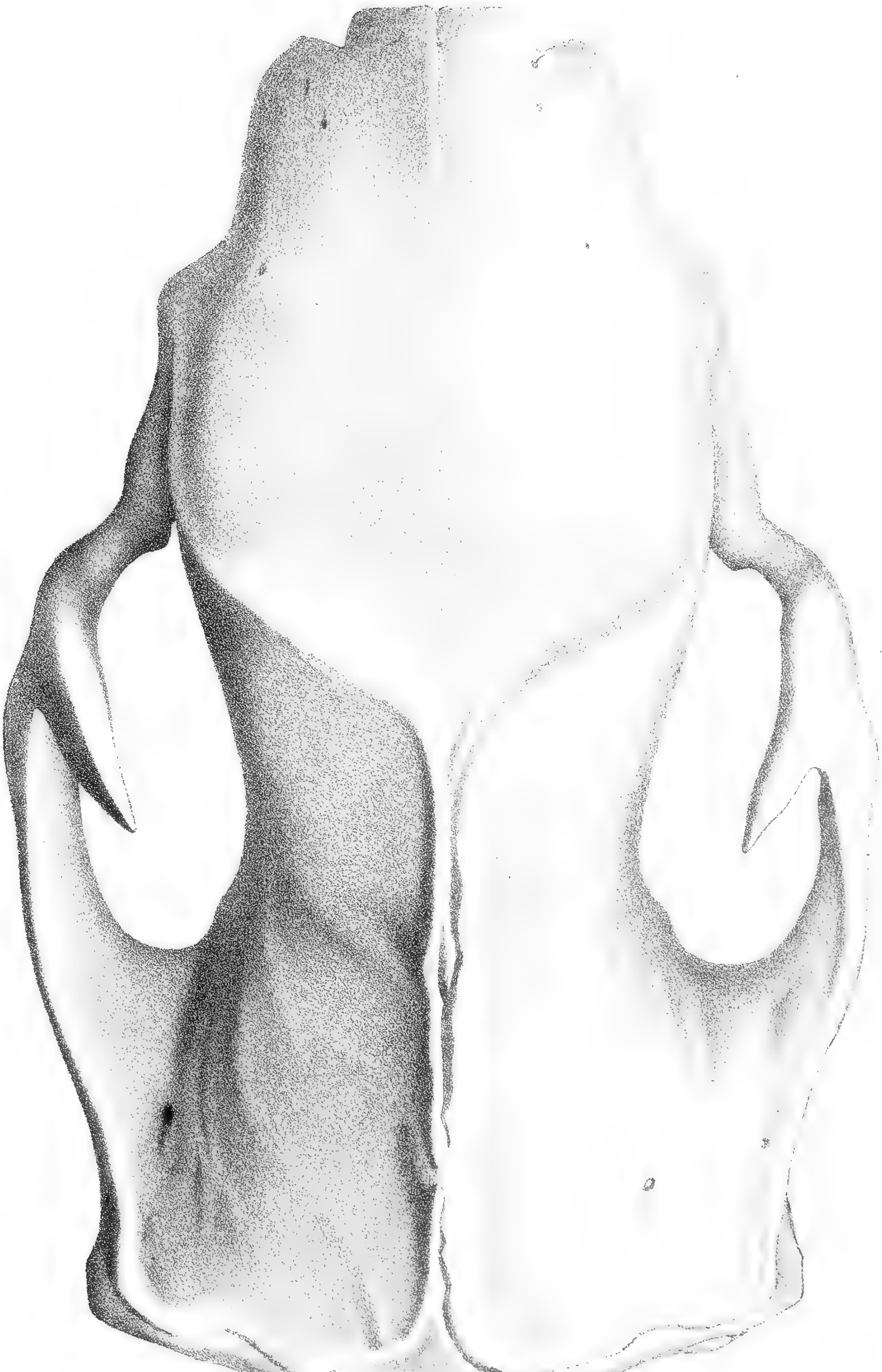
### *Plate V.*

Figs. 1, 3 and 5. Sections of skull of *M. leidyi* } (see page 7).
Figs. 2, 4 and 6. Sections of skull of *M. jeffersoni* } (see page 7).
Fig. 7. Dentition—natural size, and arranged on the plate in natural position.
Figs. 8 and 9. Views of exterior side and triturating surface of left canine molar; natural size.

P. S.—Prof. E. D. Cope, in letters to Prof. Udden, determined the teeth of *Equus major*, found in the same bed as this skull, and also determined the age of the formation as belonging to the *Equus* beds. He afterwards referred to the skull, in *Am. Nat.*, Vol. xxiii, p. 660, as "only found in the *Ticholeptus* formation of Kansas." This was a *lapsus calami* which had escaped his notice until after the above was in type, and, at his request, it is hereby corrected. His figures, Pl. xxxi, were reproductions of three photographs made in Kansas. The photographer had placed the broken left canine-molar upside down in the right (the wrong) alveole.—J. L.

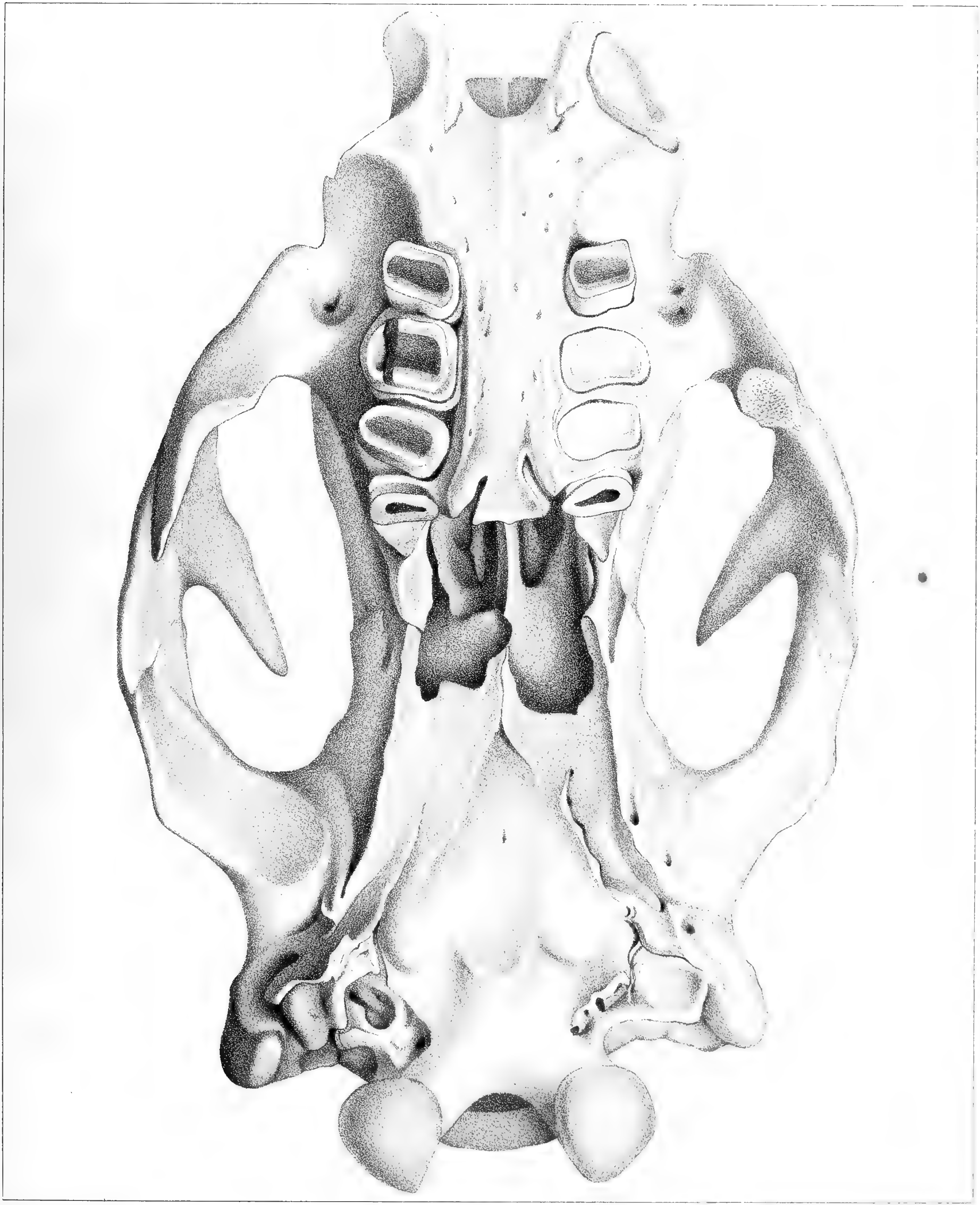
A. M. Westergren del. G. Tholander lith. W. Schlachter, Stockholm, Sweden

MEGALONYX LEIDYI Lindahl.



A.M. Westergren del. G. Tholander lith. W. Schlachter, Stockholm, Sweden.

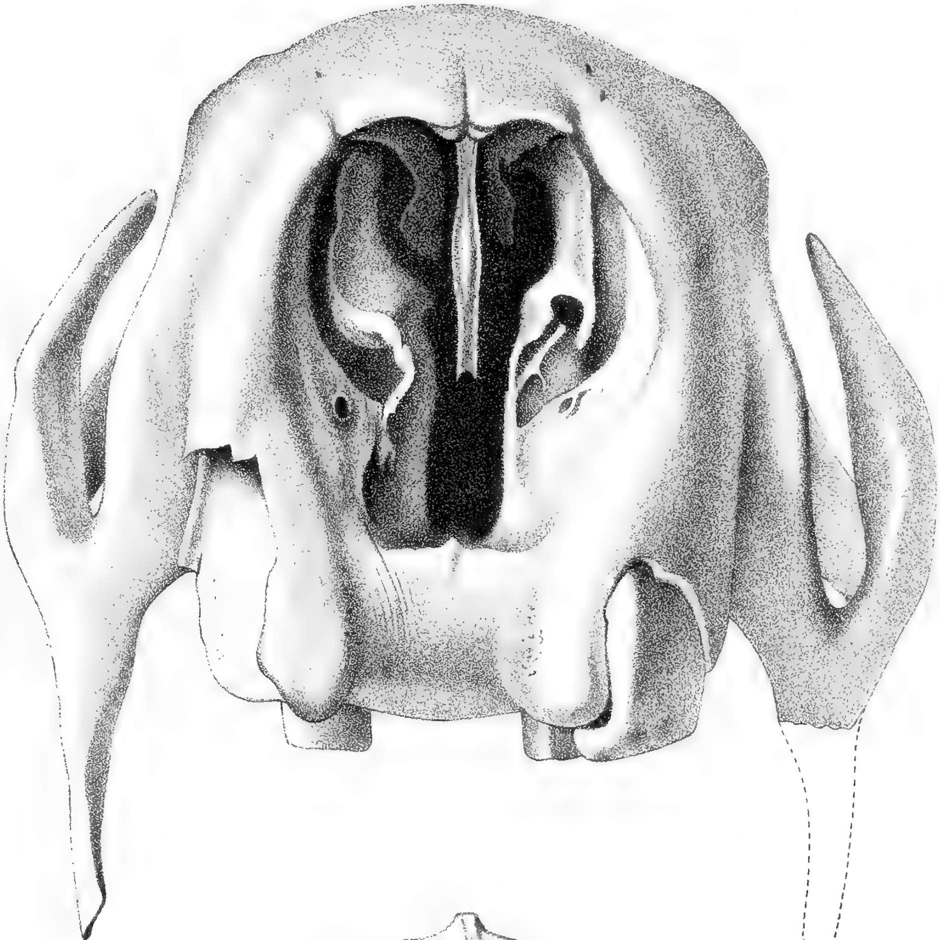
MEGALONYX LEIDYI Lindahl.



A. M Westergren del. G. Tholander lith W. Schlachter. Stockholm. Sweden

MEGALONYX LEIDYI Lindahl

*Fig. 1.*



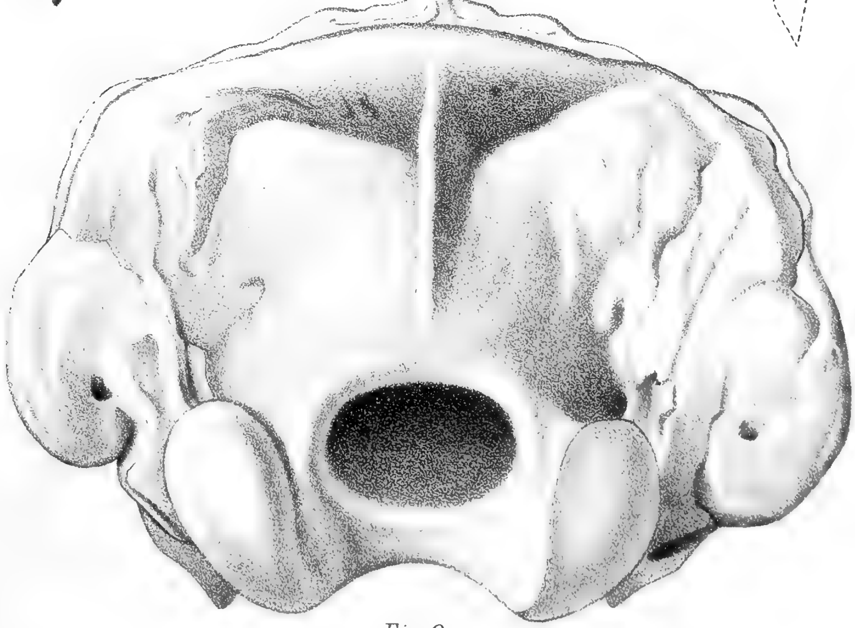


*Fig 2.*

A. M. Westergren del.

G. Tholander lith.

W. Schlachter. Stockholm, Sweden

MEGALONYX LEIDYI Lindahl.

Fig 1

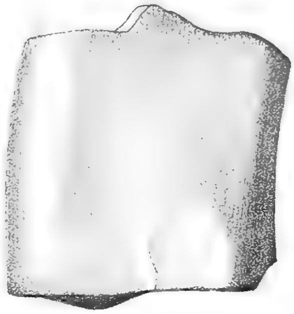


Fig. 8

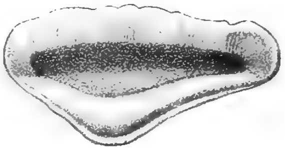


Fig. 9

Fig 2

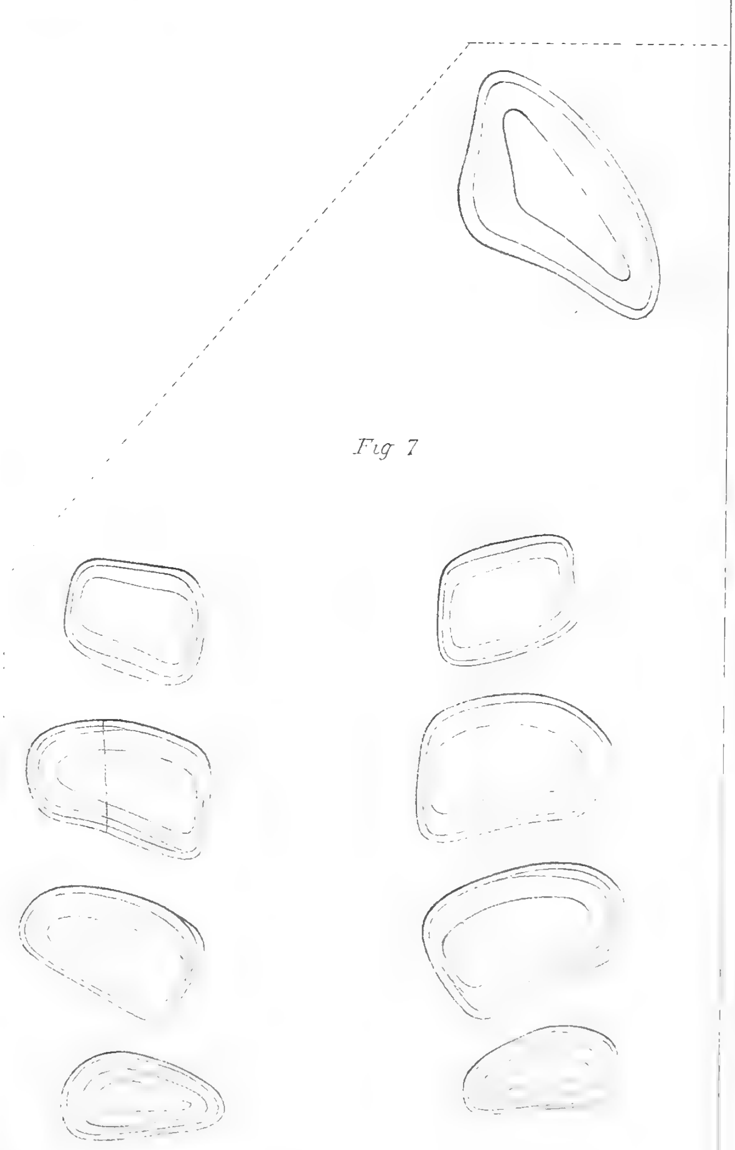


Fig 7

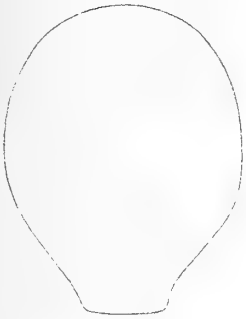


Fig 3

Fig 4

Fig 5

Fig. 6

A. M Westergren del.
G Tholander lith
W. Schlachter, Stockholm, Sweden.

Figs 1, 3, 5, 7, 8, 9 MEGALONYX LEIDYI Lindahl
" 2, 4, 6 " JEFFERSONI Harlan

### ARTICLE II.

# ON THE HOMOLOGIES OF THE POSTERIOR CRANIAL ARCHES IN THE REPTILIA.

BY E. D. COPE.

**Read before the American Philosophical Society, February 5, 1892.**

At the meeting of the American Association for the Advancement of Science, held in Troy, N. Y., in 1870, I presented the result of my studies of the arches which distinguish the posterior part of the cranium in the Vertebrata, and especially in the Reptilia. Three arches were considered, which were named, commencing with the inferior in position: the quadratojugal, the zygomatic and the parietoquadrate. Of these the only arch recognized as occurring in the Mammalia was the zygomatic.* In the determination of this arch I followed Cuvier,† and for the following reason. It was supposed that the quadrate bone represented one of the ossicula auditus. As this element in the Mammalia is intracranial, and does not give support to an arch, the zygomatic arch of that class could not be homologous with the arch which it (the quadrate) supports in the Reptilia (the quadratojugal). The zygomatic arch of the latter class would be, on the contrary, that one which originates at the proximal extremity of the quadrate, which would remain on the supposed withdrawal of the latter within the skull as one of ossicula auditus.

Prof. Peters has, however, shown that the quadrate bone is probably not one of the ossicula auditus, and he is followed by Dollo, Albrecht and others. In a study of the osteology of the Permian reptile, *Diopeus leptocephalus* Cope,‡ I came to the conclusion that the quadratojugal arch of that reptile is the zygomatic arch of the

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* Proceedings Amer. Assoc. Adv. Sci., XIX, 1870, p. 197.

† Ossemens Fossiles, X, Ed. 1836, 14.

‡ *Clepsydrops leptocephalus* Cope. Proceeds. Amer. Philos. Soc., 1884, pp. 30–42. Diopeus, gen. nov., described on a later page.

Mammalia, thus coinciding with the opinion as to the homologies of that arch held by Hallmann, Owen and Peters, and as described by Günther in Sphenodon. On further study of the Permian reptiles contained in my collection, and comparison of them with recent orders, I am more than ever convinced of the correctness of this view, and I propose in the present paper to show the evidence on which it rests. It follows, moreover, that if this interpretation be correct, the bone ordinarily called quadratojugal must be called the squamosal or zygomatic, while the bone to which that name is ordinarily applied must receive another name. The element immediately above the true squamosal, which roofs the temporal fossa in the Stegocephali and Cotylosauria, is the supratemporal of Owen,* first described by him among reptiles in Ichthyosaurus. The element immediately above the supratemporal in the Stegocephali, Cotylosauria and Ichthyopterygia is the mastoid of Cuvier and Owen. As it is probably not homologous with the part of the Mammalian skull called by that name, some other one must be found for it. The numerous names given to bones in this region of the skull all apply to the squamosal or supratemporal, so I propose to name this one the *supramastoid.*

Posterior to the supramastoid in the Stegocephalian and in some of the Cotylosaurian skulls, is an element which frequently projects in an angle in the posterior outline, and which corresponds with the element present in the fishes, which Cuvier termed the intercalare. The relation of this piece to the paroccipital of certain reptiles remains to be ascertained.

It is evident that the correct classification and phylogeny of the Reptilia will not be completed without the determination of the homologies of these segments, and the homologies of the arches to which they contribute. In the endeavor to accomplish this analysis I have been much aided by a suggestion made by Dr. George Baur, which has been fertile of valuable results. In a recent paper† he says: "In the oldest Batrachia, the Stegocephalia, we find a continuous dermal covering of the upper and lateral parts of the skull; * * * the number of these dermal ossifications is nearly constant. * * * The complete covering of the skull is for the first time interrupted in the Ichthyosauria and Aëtosauria‡ by the appearance of a supratemporal fossa, which develops between the parietal, squamosal and the upper posterior border of the orbit. The bony arch below the supratemporal fossa, which connects the orbit with the quadrate, is now affected in two different ways: I. The

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*Suprasquamosal of Owen is the same; see Palæontology, pp. 168, 174, 198. Seeley uses the term supratympanic for the same.

†American Journal of Morphology, 1889, p. 471.

‡Or Pseudosuchia.

broad single arch remains single, but becomes more and more slender and can be interrupted. Plesiosauria, Theromora, Mammalia, Squamata (Lacertilia, Pythonomorpha, Ophidia). II. In the broad single arch appears another opening, the infratemporal fossa, forming an upper and lower arch which connects the orbit with the quadrate; Rhynchocephalia; the whole Archosaurian branch (Crocodilia, Dinosauria, Pterosauria); birds." Dr. Baur then proceeds to identify the postorbital arch of the Lacertilia with the quadratojugal or zygomatic arch, expressing the belief that the ancestors of that order never possessed any other quadratojugal arch, and that the present elevated position of the arch in the Lacertilia is due to reduction at the inferior border. Thus the supratemporal of the lizards (squamosal Auct.) would be the equivalent of the quadratojugal of Sphenodon.

In the endeavor to reach a definite conclusion regarding these questions, I have examined my specimens of the Reptilia of the Permian formation, as being most likely to furnish essential facts. I now give the results of this examination.

## I. The Reptilia of the Permian.

I have well-preserved crania which display sutures of the following species: *Chilonyx rapidens* Cope; *Pantylus cordatus* Cope; *Pariotichus megalops* Cope; *Edaphosaurus pogonias* Cope; *Clepsydrops natalis* Cope; *Naosaurus claviger* Cope; *Diopeus leptocephalus* Cope.

The genera Chilonyx, Pantylus and Pariotichus have the temporal fossæ entirely roofed over, thus belonging to the Cotylosauria,* to which must be probably referred the genus Pariosaurus Owen, of the South African Karoo formation, and the Phanerosaurus of the German Permian. The other genera, excepting Diopeus, belong to the Pelycosauria, which is probably the same as the Theriodonta of Owen.

Chilonyx† agrees with the Stegocephalia, and with other Diadectidæ in possessing a distinct *os intercalare.* The component elements of the cranial roof are equal in number and similar in position to those of the Stegocephalian skull, except that the supramastoid extends between the parietal and intercalare to the posterior border of the cranial table (Fig. 2, *Sm.*); and the supraoccipital does not extend onto the superior face of the skull, except as a narrow border. The quadrate bone is directed forwards instead of posteriorly, which causes an anteroposterior abbreviation of the supratemporal and squamosal elements. The elements of the temporal roof

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* Cope. American Naturalist, 1880, p. 304; October, 1889. Pariosauria Seeley. Philos. Transac., London, 1889, p. 292.

† Cope, Proceed. Amer. Philos. Soc., 1883, p. 631.

are not exclusively tegumentary, but are identical in character with the bones of the brain case, and the sutures are visible on the under as well as the upper side.

PANTYLUS* agrees with Chilonyx in the composition of its cranial roof with the exception that the suspensorium is vertical and is not directed forwards. The position of the supraoccipital and intercalare cannot be ascertained, owing to the condition of the specimens (Fig. 4, Plate I).

PARIOTICHUS Cope† agrees in the main with Chilonyx, but the supraoccipital is divided medially and is reflected onto the superior face of the skull as in Stegocephali. The intercalare is reduced to a small element, of which a small part appears on the superior face of the skull immediately behind the exterior part of the supramastoid (Fig. 3, Plate I).

It is then these three genera which, according to Baur's theory, represent the type from which the reptiles with posterior cranial bars have been derived by the development of foramina in the temporal roof. Let us see how this has been accomplished in the different types. I commence with the Permian genera.

The Theriodont genus, from the Permian of which I possess the best preserved cranium, is NAOSAURUS Cope (Fig. 7). It is, unfortunately for our purpose, the most extremely modified. The orbit is in the posterior part of the skull, and the muzzle is greatly elevated and compressed. The zygomatic (quadratojugal) is greatly decurved posteriorly, and the supratemporal is accordingly decurved also. The postfrontal (Fig. 7*a*) is a narrow bone, wider than long, and it has connection with the frontal, parietal and postorbital only. The postorbital is an L-shaped structure, of which the shorter limb is inferior, extending to the jugal, while the longer limb is posterior, extending to the supratemporal, in contact with the parietal. It encloses no foramen with the latter; but it encloses a larger foramen with the jugal, zygomatic and supratemporal at the other boundaries. This is the infratemporal foramen of Baur. Posterior to the parietal is a small transverse element, which appears to be merely adherent to the former. Its determination is not easy at present. The supratemporal is elongate vertically, and narrow anteroposteriorly. Beneath and towards the middle line of the skull is a part of another bone, which may be the paroccipital, or even exoccipital. The pineal foramen is distinct. No parietoquadrate arch.

In CLEPSYDROPS‡ the structure is apparently the same, although the form is much less modified. The quadrate articulation is nearly in line with the maxillary dental series (Fig. 6, Plate II), and the jugal is nearly horizontal; its inferior border

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* Cope, Bullet. U. S. Geol. Survey Terrs., 1881 (8vo).

† Proceeds. Amer. Philos. Soc., 1878, p. 508.

‡ Cope, *loc. cit.*, 1878, p. 509.

being concave upwards. No bar extends posteriorly from the postorbital, which joins the supratemporal, enclosing with it the infratemporal foramen. No indication of the supratemporal foramen can be found in the rather mutilated specimen. I think it was not present.

In EDAPHOSAURUS Cope (Fig. 5, Plate II), the skull is of a more depressed type than in the preceding genera. The postorbital is mainly preserved, and it is in contact with the frontal (postfrontal) proximally, and sends out no bar posteriorly. There was apparently no supratemporal foramen, but a very large infratemporal, which extended well upwards. There is no parietoquadrate arch. An element, perhaps supraoccipital, terminates in a free appressed apex on each side of the median posterior region. This may be homologous with the small free bone described in Naosaurus, in nearly the same position. The stapes is very large, and is at least partially perforated near the expanded proximal extremity. It is probably fully perforated, as I have described it in the *Diopeus leptocephalus* Cope.

In DIOPEUS Cope, the supratemporal is elongate in the vertical direction, and as elsewhere, it overlaps the quadrate at the distal extremity. Anteriorly, it sends forwards a process probably for union with the postorbital bone, which is, however, entirely free from the parietal, and encloses a foramen with it, precisely as in Sphenodon. It further resembles the corresponding element in Sphenodon in sending upwards a branch for union with the parietal. Thus there are in this genus two posterior bars and two foramina, thus differing widely from the other Permian genera of this or any other country known to me. Whether it has a free parietoquadrate arch I do not know, but it is probable that the genus should be referred to the Rhynchocephalia, in the neighborhood of Palæohatteria Cred. It differs from Sphenodon and resembles closely the Theriodonta in the absence of an obturator foramen, and in the character of its dentition.* The zygomatic bone is not excavated below, but has a straight outline to its junction with the jugal. The quadrate condyle is double like that of Sphenodon and the Clepsydropidæ (Fig. 8, Plate II).

The THERIODONTA described by Owen appear to have the single cranial arch constructed in the same way as I described above as characteristic of the American forms. I gather this from Owen's figures of the genera Kistecephalus Ow., Galesaurus Ow., Scaloposaurus Ow., Anthodon Ow., and apparently Lycosaurus Owen.

The ANOMODONTA appear to have a differently constructed posterior cranial region. In my study of the skull of Lystrosaurus Cope† (Proceeds. Amer. Ass. Adv. Sci., 1870, XIX, p. 205), I showed that this genus possesses an extensive supra-

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* Proceeds. Amer. Philos. Soc., 1884, p. 33.

† Ptychognathus Owen (preoccupied) ; Ptychosiagon Lydekker, 1889.

temporal foramen, and that the bone which bounds it externally consists posteriorly of the supratemporal bone, and not the zygomatic. Anteriorly this bone joins the postorbital, postfrontal and malar. In the Transactions of the Royal Society for 1889, p. 244, Prof. H. G. Seeley analyzes the structure of the skull of Dicynodon, which he shows to resemble closely that of Lystrosaurus, and his analysis of the posterior arch and foramen is the same as my own in the latter genus. It is evident then that the Anomodonta differ from the Theriodonta in the absence of a zygomatic arch, and in the presence of a supratemporal arch, which is separated from the parietal bone by a supratemporal foramen (Figs. 1–2).

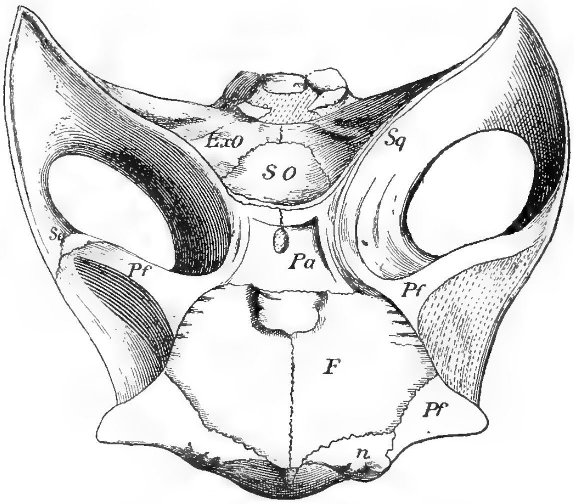

FIG. 1.

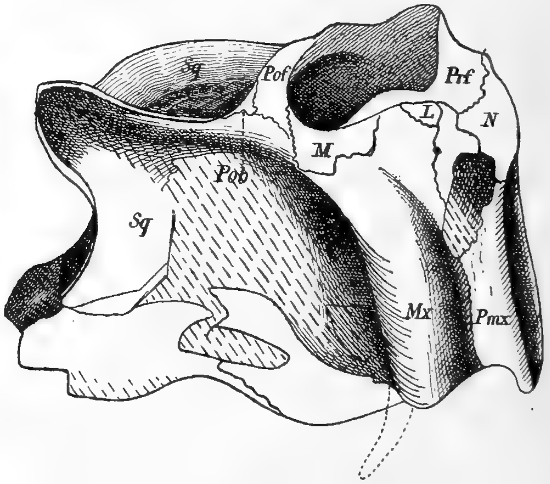

FIG. 2.

Fig. 1. *Lystrosaurus frontosus* Cope. An Anomodont from South Africa; skull from above. Fig. 2, do., from right side. The lower *Sq* is the supratemporal.

The South African genus **Procolophon** Ow. has been analyzed by Seeley* in an admirable manner. The orbit is greatly enlarged, so that the region of the bars is contracted. However, there is a zygomatic arch, an infratemporal foramen, and no supratemporal foramen, thus agreeing with the Theriodonta, and not with the Anomodonta.

In conclusion it appears that there are four types of crania represented in the Permian Reptilia, which are distinguished as follows:

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|---|---|
| Temporal roof uninterrupted | *Cotylosauria.* |
| A zygomatic arch, but no distinct supratemporal or supramastoid arches | *Theriodonta.* |
| Zygomatic and supratemporal arches | *Diopeus.* |
| No zygomatic; a supratemporal arch | *Anomodonta.* |

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* Philos. Trans. Roy. Soc., 1889, p. 269.

## II. The Mesozoic Reptilia.

We may now examine how far the cranial types above described continued into Mesozoic time, and ascertain whether any new forms appeared.

In the first place, Aëtosaurus Fraas presents a single foramen perforating an otherwise continuous roof of the temporal fossa. This foramen is bounded below by the postorbital and supratemporal bones. The postfrontal bone is closely joined to the parietal, and has no posterior extension except to the postorbital. The zygomatic arch is present and is continuous with the supratemporal and postorbital bones, there being no infratemporal foramen. These details are derived from Fraas' figures copied by Zittel in his Handbuch der Paleontologie.* In this figure no distinct zygomatic (quadratojugal), or supramastoid, is visible, but whether they are wanting or fused with adjacent elements, examination of specimens will best show. This genus is made the type of a suborder of Crocodilia by Baur (Pseudosuchia), but it appears to me to be typical of a special order (Pl. IV, Fig. 2).

The genus Ichthyosaurus presents especial features. Here we have a zygomatic arch, and no infratemporal foramen. There is a superior foramen, however, which is bounded below by the postfrontal bone in front, and the supramastoid behind; which are themselves in contact below with the postorbital and the supratemporal. This foramen I call the supramastoid. A paroccipital bone is present in this genus, but no intercalare. See my memoir of 1870 above referred to (Pl. V, Fig. 1).

The Dinosauria may be represented by Diclonius, of which I have a complete skull before me (Pl. III). Here there are superior and inferior foramina which isolate two arches, of which the inferior is the zygomatic. The superior arch consists of the supramastoid bone posteriorly, and apparently the postfrontal anteriorly. The supratemporal, small in Ichthyosaurus, has now disappeared. There is a distinct paroccipital lying scale-like on the exoccipital. In Diclonius the supramastoid is fused with the parietal,† but in Iguanodon, according to Dollo, it is distinct.‡ The fact that the postfrontal and postorbital are not distinct from each other in the Dinosauria with which I am acquainted, makes the determination of the character of the superior arch somewhat difficult. This is probably the case in Diclonius, and is so represented by Dollo in Iguanodon. In a fine cranium of the Laramie *Lœlaps incras-*

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* Page 644, Fig. 569.

† Cope. Proceeds. Acad. Phila., 1883, p. 110, Pl. V. In this description and plate the sutural lines supposed to separate the postfrontal from the postorbital and "squamosal" are of doubtful existence in the specimen.

‡ Bulletin de Musée Royale d'Histoire Naturelle de Belgique, II, 1883, p. 235, Pl. II.

*satus* Cope,* I find the bone in front of the arch to form two limbs of a nearly right-angled triangle, one of which is supraorbital, and the other postorbital. No suture divides it. It may represent the fused postfrontal and postorbital elements which we have in some Lacertilia. There is, however, a small free bone horizontally placed at the internal side at the posterior extremity of the supraorbital limb, which may be a postfrontal bone. In this case the anterior connection of the supramastoid bone will then be with the postorbital. This must however be clearly proven before it can be accepted, since it is the postfrontal bone † which articulates with the supramastoid posteriorly. If we suppose the long perpendicular postorbital process of the bone in question to represent the postorbital bone of Ichthysaurus, the question is simplified, but it is not certain that such is the case.

The figures given by Marsh of the "*Ceratosaurus*" *nasicornis* represent a structure similar to that of Lælaps, and similarly indecisive. The figures of *Hypsirhophus stenops*‡ (Stegosaurus Marsh) exhibit distinct postfrontal and postorbital bones. They show the postorbital produced upwards and backwards to form the horizontal bar with a posterior element. Between this element and the parietal is represented on one side of the figure another element, but this entire region is left undescribed in the text. The appearance given by one side of the figure (3) is that the supramastoid and supratemporal are both present, and that the latter is the posterior element in the bar. In that case the structure is that of the Theriodonta and Lacertilia, and not that of the Ichthyosauria.

The situation in the CROCODILIA appears to be the same as in the Dinosauria. Nothing satisfactory can be learned from the recent members of the order; and even in the skull of an *Alligator mississippiensis* one inch long, the postfrontal and postorbital bones are not distinct from each other. The Jurassic forms of the Teleosauridæ show the same character, and give the appearance of a postorbito-supratemporal arch.§ In the Triassic Belodon the structure seems to be essentially similar. The appearance in the PTEROSAURIA, as figured by authors, is the same as in the Dinosauria, but I cannot pronounce decisively in the lack of specimens. It is not unlikely that all the members of the Archosaurian series resemble each other in this respect, and I suspect that it is to be explained by reference to the Theriodonta. Here the postfrontal and postorbital are distinct, as already pointed out, but the former is small and is crowded by the adjacent elements. Its fusion with the post-

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* Which I owe to the Geological Survey of Canada.

† Including the supposed squamosal of my description of Diclonius (*l.c.*).

‡ Amer. Jour. Sci. Arts., 1887, Pl. VI.

§ See Eudes Deslongchamps Notes Paleontologiques, 1863–9.

orbital would be probable. The arch is then supratemporal, and this element may be fused with the supramastoid in the Dinosauria.

If the Rhynchocephalia of the Mesozoic had the same structure as Sphenodon, we may ascribe to them an infratemporal foramen and a zygomatic arch. The former is bounded above by a bar which consists anteriorly of the postorbital, and posteriorly, in all probability, of the supratemporal. Hence the postfrontal and supramastoid do not communicate as they do in the Ichthyopterygia; and the large foramen above the superior bar has different boundaries below from that observed in Ichthyosaurus, but is like that of the Anomodonta. Hence I call this foramen the supratemporal foramen, and the bar the supratemporal bar. In Sphenodon the paroccipital and supratemporal are fused together. The supramastoid is fused either with the supratemporal or the parietal (Fig. 9, Pl. II, and Fig. 3, Pl. IV).

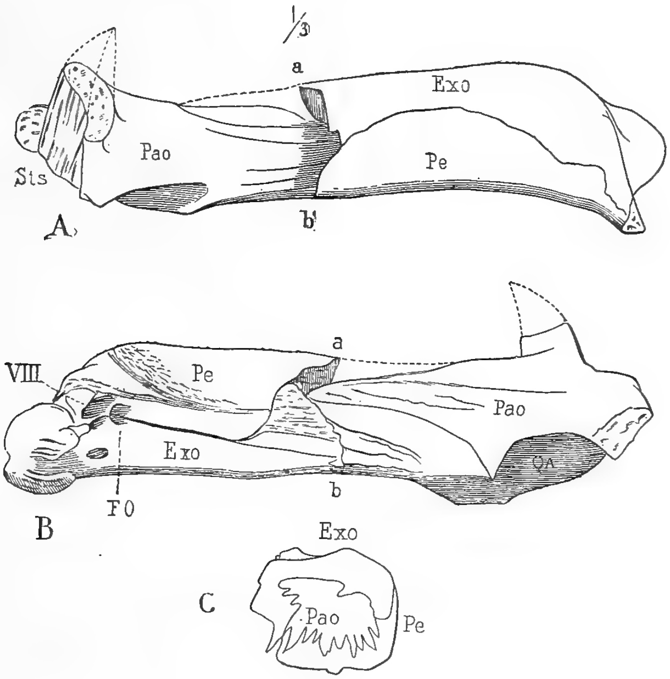

FIG. 3.

Fig. 3.—Mosasaurus sp., suspensorium of *os quadratum* of right side, one-third nat. size; from Greensand of New Jersey. *A*, from front; *B*, from behind; *C*, fractured end of proximal half seen at fracture, *a–b*; *Exo*, exoccipital; *Pe*, petrosal; *Pao*, paroccipital; *Sts*, suture for supratemporal; *QA*, articular surface for quadrate; *FO*, fenestra ovale; *VIII*, foramen for eighth nerve; *a b*, line of fracture.

In the Pythonomorpha and Lacertilia the zygomatic arch of the Rhynchocephalia has disappeared, leaving the superior or supratemporal arch only. That this is truly the supratemporal arch and not the supramastoid is shown by the fact that its anterior connection is with the postorbital as in Sphenodon, and not with the postfrontal. I cannot agree with Baur that this arch in the lizards is the zygomatic arch of the other Reptilian orders. The supramastoid bone is, in the Lacertilia, wanting, but whether by atrophy or by fusion with the parietal, forming the supramastoid process of the latter, I do not know. An element intervenes between the supratemporal bone and the parietal above and the exoccipital within, which Dr. Baur regards as the supratemporal. With this I do not agree, and for the following considerations: In neither adult nor young Lacertilia is there present any other element which can be regarded as the homologue of the paroccipital of Ichthyosaurus, the Testudinata and Dinosauria. In the Pythonomorpha this element is deeply embraced between the petrosal (proötic) and exoccipital, precisely as is the paroccipital (Fig. 3). In the Lacertilia it is carried on the extremity of these elements. Moreover the supramastoid is a purely roof-bone, and has no connection primitively with the petrosal, and very little with the exoccipital. It cannot be identified with the supratemporal because it exists contemporaneously with that element in Ichthyosaurus,* as well as in the Cotylosaurian genera Chilonyx and Pariotichus above described. I therefore maintain the homology of this bone with the paroccipital as I presented it in my paper of 1870, where I used for it Huxley's term "opisthotic." (Pl. IV, Fig. 5). Parker, in his paper on the Development of the Skull in the Lacertilia,† did not discover a distinct ossification in the position of paroccipital, although he finds a portion of the exoccipital marked off by a shallow groove, which he calls opisthotic. The true paroccipital he calls the "second supratemporal."

In the Ophidia there is no zygomatic or supratemporal arch, and the supratemporal as well as the supramastoid bones have disappeared. The paroccipital is the only one of the suspensors of the quadrate remaining. This element had been generally homologized with the "squamosal" (supratemporal) by authors, but in my paper of 1870 I identified it with the paroccipital of the Lacertilia ("opisthotic;" supratemporal of Baur), with which Baur agrees. In the more specialized snakes its squamosal attachment to the cranial wall resembles that of the squamosal bones of higher Vertebrata, and its general position is that of that element. When, however, the lower snakes, *e.g.*, Ilysia, are examined, it is found to have the same position in the embrace of the exoccipital and petrosal bones, as in the Pythonomorpha, and to be clearly homologous with that element which I have thought to be the paroccipital (Pl. IV, Fig. 6).

In the Testudinata, as pointed out by Baur, no foramina have been devel-

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* The process of the parietal which joins the supramastoid arch in Diclonius (Plate III) may represent the supratemporal.

† Philosophical Transactions Royal Soc., 1879, p. 631.

oped, but the primitive roof has suffered diminution by absorption from the inferior edge, or from both the inferior and the posterior edges. In Chrysemys, where a bar has been produced (Pl. V, Fig. 5), it consists of the unseparated zygomatic and supratemporal, the anterior elements of which are the jugal and postorbital; and the posterior, the zygomatic and supratemporal. The supramastoid is wanting even in the genera (Hydraspis *e. g.*) with a parietoquadrate arch. The postfrontal and postorbital are not distinguished. In genera, where the posterior excavation is very deep (*e. g.*, Trionyx), the connection between the postorbital and the supratemporal is interrupted, and a zygomatic arch remains (Pl. V, Fig. 6). It was comparison of this type with the Lacertilia that led Baur* to conclude that the bar of the latter order is the zygomatic.

The SAUROPTERYGIA possess but a single arch, and this is the zygomatic according to the description of Nothosaurus given by Von Meyer. The supratemporal has no anterior connections according to this author, and the supramastoid is not described. From all that I can gather from Owen's descriptions and figures of Plesiosaurus the structure is the same; which is confirmed by observation on such imperfect specimens as are accessible to me. The postfrontal is not continued above the large temporal foramen; nor is the postorbital continued posteriorly. In the latter point the structure differs from that of the Theriodonta. The type of the Sauropterygia may be derived from that of the Theriodonta by the extension of the infratemporal foramen upwards to the parietal bone, thus cutting off the posterior connections of the postorbital and postfrontal bones. In this respect this type resembles the Testudinata (Pl. V, Fig. 4).

The Mesozoic reptiles (including the existing orders) present us then with the following types of postorbital structure:

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|---|---|
| I. One foramen; generally a zygomatic arch. | |
| No supramastoid bone; postfrontal and postorbital fused; a paroccipital | *Testudinata.* |
| Postfrontal and postorbital distinct | *Sauropterygia.* |
| II. A supramastoid foramen only. | |
| Supramastoid and zygomatic arches not distinguished from each other; a paroccipital, | *Ichthyopterygia.* |
| III. A supratemporal and infratemporal foramina. | |
| Supramastoid and zygomatic arches | *Crocodilia.*<br>*Dinosauria.*<br>*Pterosauria.*<br>*Rhynchocephalia.* |

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* Amer. Journal of Morphology, 1889, p. 473.

IV. A supratemporal foramen only.

Zygomatic and supratemporal arches present and not separated by an infratemporal foramen, *Pseudosuchia.*

A supratemporal and no zygomatic arches; a paroccipital .......................... *Lacertilia.* *Pythonomorpha.*

V. No arches or foramina.

Quadrate suspended to paroccipital .................................................. *Ophidia.*

These structures must be considered in determining the systematic position of the groups above enumerated, but their characters are not all of equal systematic value.

## III. The Parietoquadrate Arch.

This arch is not present in the Batrachia, and is very variously developed in the Reptilia. It is produced by the separation of the posterior elements of the temporal roof of the Stegocephali and Cotylosauria, from the elements of the brain case below them. That is, by the development of a foramen between the supramastoid and supratemporal above, and the exoccipital and paroccipital below.

The parietoquadrate arch is a later appearance in geologic time. It is not present in any of the Permian orders. The earliest indication of it is seen in the Ichthyopterygia, where a space appears between the very large supramastoid above, and the exoccipital and paroccipital below. It is wanting in the three Archosaurian orders, but is represented by a fissure in the Triassic Belodon, and in Crocodilia in general.* In Testudinata it is potentially present in the posterior part of the temporal roof, but is only distinguished in certain Pleurodira (Hydraspis), where the supramastoid element is lost, or fused with the parietal processes which form its proximal part. In the Rhynchocephalia it is well developed in Sphenodon, but here also the supramastoid element is not distinct, being fused with either the supratemporal or parietal. The arch has the same character in Lacertilia, except that the paroccipital sends upwards a brace along its inferior border. That this element is the paroccipital has been already shown by reference to the structure in the Ichthyosaurus and in the Pythonomorpha (Fig. 3).

The space enclosed below the parietoquadrate arch I propose to call the parietoquadrate foramen. Its presence is an indication of systematic value, but not in general of a high grade. Thus among the Squamata it is absolutely wanting in Ophidia, and is scarcely elevated above the exoccipital in some Pythonomorpha. In Lacertilia the foramen is much reduced in Feylinia, and is wanting in Anniella and the Amphisbænia, while it is large in most other types.

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* See Deslongchamps, E., Notes Paleontologiques, I, 1868–9, Caen et Paris.

## IV. Systematic Considerations.

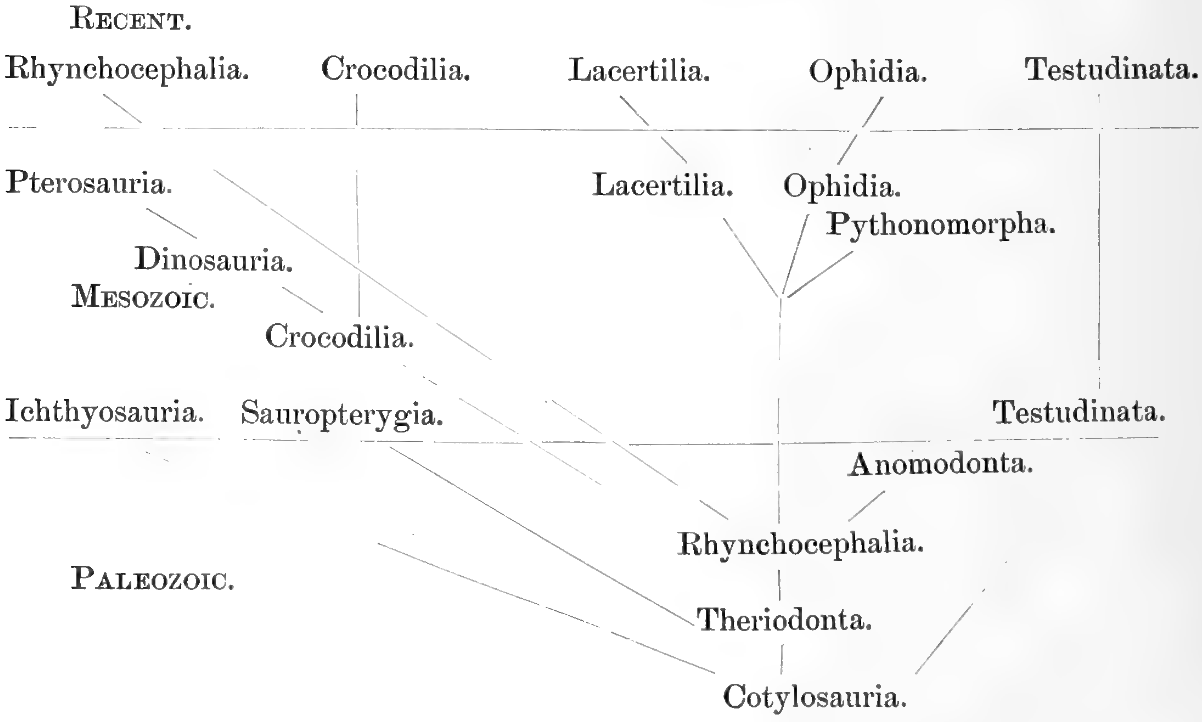
From the preceding facts certain results follow. The knowledge of the Permian types enables us to trace the affinities of the orders of later ages with much more precision than has been possible hitherto. In the first place, we derive the Testudinata directly from the Cotylosauria, which realizes the theoretical type which Baur correctly supposed to have given origin to all the later orders. Thus we need not look for the ancestry of the Testudinata in any other group. This order then constitutes Series I.

As Series II we can take up the line in which the supramastoid foramen appears (Ichthyopterygia). This type is not clearly marked out in the Permian, but according to Baur the Triassic Mixosaurus presents an approximately terrestrial form of Ichthyosauria, which can be probably traced to Permian ancestors. This series does not seem to have been continued, but this is not to be assumed, as yet, without further evidence.

As Series III we commence with the Permian Theriodonta, where an infratemporal foramen is first developed. In Diopeus a supratemporal foramen appears. The latter represents the type of the Rhynchocephalia, and probably the Dinosauria, Crocodilia and Pterosauria. The loss of the supratemporal bar and preservation of the zygomatic gives us the Sauropterygia. The loss of the zygomatic arch only, gives us the Anomodonta; and the non-sutural articulation of the quadrate gives us the Squamata. The loss of both the supratemporal and zygomatic bars gives us such Lacertilia as Heloderma and Anniella, and the Ophidia.

The importance of the connections of the posterior bars of the skull is for the first time appreciated in the present paper. It is difficult to learn these connections from the writings of authors, so completely have they been neglected. For instance, the terms postfrontal and postorbital are sometimes used indifferently by Marsh in describing the crania of Dinosauria. It is true that in a few Lacertilia, as the Varani, these elements are fused together. The supramastoid and supratemporal elements have been generally confused except in the Ichthyosauria, where both exist together. It may be alleged that the difference between the supramastoid and supratemporal bars is not great, and that the one might have been readily transformed into the other. But this supposition will not bear examination. When the one bar has been established the other has been lost, and a recovery after such loss is not probable. This follows from the fact that the position of a bar is the result of the loss of the Cotylosaurian roof from all other regions. The only case where the reduction has not at first restricted the roof to the position of one bar or the other, is that of the Testudinata, where both sets of elements are included in a single bar. This compound bar is, however, reduced to the zygomatic elements in the more specialized forms, and is not unfrequently entirely lost.

Aided by these considerations we get the following phylogenetic series. Each one of them originated in the Permian epoch. This table resembles essentially the one I gave in the article on the Evolution of the Vertebrata in the American Naturalist for 1885, p. 247, in which all the later orders were traced to the Theromora, the Lacertilian series through the Rhynchocephalia. The varied character of that assemblage was not at that time suspected, but it is true that there is a great resemblance between the orders now included in it, except in the matter of the cranial roof and bars, and in the nature of the rib-articulations. The discovery that Diopeus is allied to the Rhynchocephalia places that order in immediate relation with the Theromorous series on the one hand; while a correct estimate of its cranial structure places it in immediate relation with the Lacertilia on the other.



The five reptilian series might be then further defined as follows:

| | |
|---|---|
| Quadrate fixed; no supramastoid or supratemporal foramen or separate arch | *Theromora.* |
| Quadrate fixed; a supramastoid foramen and arch | *Ichthyopterygia.* |
| Quadrate fixed; a supratemporal and zygomatic arch | *Archosauria.* |
| Quadrate fixed; a zygomatic arch only | *Synaptosauria.* |
| Quadrate free; no supramastoid foramen or arch; a supratemporal but no zygomatic arch. | *Streptostylica.* |

The Theromora are the earliest in time, and their order of Theriodonta presents the nearest affinities to the Mammalia. The Cotylosauria, on the other hand, display the nearest relations to the Stegocephalous Batrachia.

In the following illustrations the phylogenetic successions are indicated by diagrams based on the skull of *Pantylus cordatus.* This is adopted as the most convenient of the Cotylosaurian types to be taken as a standard, because it displays none of the especial peculiarities that characterize Chilonyx, and is better known in the lateral posterior region than Pariotichus. In the series which terminates in the Streptostylica we commence with the Theriodont type in Fig. 1, with an infratemporal foramen only, and reach Diopeus or Sphenodon with both infratemporal and supratemporal. This is naturally followed by Dicynodon with supratemporal foramen and no zygomatic arch, from which we pass to the Lacertilia, which has the free os quadratum. The descent of the Lacertilia is from the Theriodonta through the Rhynchocephalia, the Anomodontia being a lateral branch. The Archosaurian line may commence with a form with a supramastoid foramen only, or one with an inframastoid only. We know no type of the latter kind; and of the former we have the aquatic Ichthyopterygia. A terrestrial type of this order probably existed, which represents the stock from which the Archosaurian line is derived. In this series the order of development probably has been Crocodilia, Dinosauria, Pterosauria, as represented in Figs. 9 and 10, Pl. V.

## EXPLANATION OF PLATES.

### *Plate I.*

STEGOCEPHALI AND COTYLOSAURIA.

*Fig.* 1. *Mastodonsaurus giganteus* Jaeger, $\frac{1}{8}$ nat. size; from Fraas.

2. *Chilonyx rapidens* Cope, $\frac{3}{8}$ nat. size; from above; premaxillary, maxillary, jugal and zygomatic regions restored; *a*, left side. Coll. E. D. Cope.

3. *Pariotichus megalops* Cope, $\frac{3}{2}$ nat. size; zygomatic region imperfect; from above; *a*, left side. Coll. E. D. Cope.

4. *Pantylus cordatus* Cope, $\frac{3}{4}$ nat. size; occipital region imperfect; from above; *a*, right side. The line passing through the postorbital, postfrontal and supratemporal is a fracture of the osseous roof. Coll. E. D. Cope.

### *Plate II.*

THERIODONTA AND RHYNCHOCEPHALIA.

*Fig.* 5. *Elaphosaurus pogonias* Cope, $\frac{3}{8}$ nat. size; with imperfect zygomatic region, seen obliquely from above; *a*, posterior view. Coll. E. D. Cope.

6. *Clepsydrops natalis* Cope, $\frac{3}{4}$ nat. size; with superior posterior part of skull imperfect; left side. Coll. E. D. Cope.

*Fig.* 7. *Naosaurus claviger* Cope, $\frac{1}{4}$ nat. size; muzzle and lower jaw wanting, but restored from allied species; zygomatic arch partly wanting; left side; *a*, from above. Coll. E. D. Cope.

8. *Diopeus leptocephalus* Cope, $\frac{1}{2}$ nat. size; supratemporal, zygomatic and quadrate bones; left side. Coll. E. D. Cope.

9. *Sphenodon punctatum* Gray, skull $\frac{3}{4}$ nat. size; right side. Coll. E. D. Cope, from Sir James Hector, New Zealand.

## *Plate III.*

Diclonius mirabilis Leidy; skull about one-fourth natural size, from side and above.

## *Plate IV.*

Diagrams of Skulls of the Theromoro-streptostylicate series; vertical and side views, based on *Pantylus cordatus.*

*Fig.* 1. Theriodonta. *Fig.* 2. Pseudosuchia (from Zittel). *Fig.* 3. Rhynchocephalia. *Fig.* 4. Anomodontia. *Fig.* 5. Lacertilia. *Fig.* 6. Ophidia.

The supramastoid-parietal suture is omitted in the Pseudosuchia to resemble Aëtosaurus. The supratemporo-supramastoid suture is omitted in the Rhynchocephalia in imitation of Sphenodon. All the teeth but one are omitted from the Anomodonta, in imitation of Dicynodon.

## *Plate V.*

The Archosaurian and Synaptosaurian Series; Diagrams of Skulls, based on *Pantylus cordatus.*

*Fig.* 1. Ichthyosauria. *Fig.* 2. Crocodilia (Teleosaurus). *Fig.* 3. Dinosauria (Diclonius). *Fig.* 5. Sauropterygia (Nothosaurus). *Fig.* 5. Testudinata (Chrysemys). *Fig.* 6. Testudinata (Trionyx).

In the Crocodilia and Dinosauria the supratemporal is omitted, and in Sauropterygia it is fused with the supramastoid. In Testudinata the supramastoid is omitted. In Dinosauria the postorbital and postfrontal are represented as fused, although this may be an appearance only.

## EXPLANATION OF LETTERING.

*Pmx.*, premaxillary bone; *Mx.*, maxillary; *J.*, jugal (malar); *Z.*, zygomatic (quadratojugal); *L.*, lachrymal; *N.*, nasal; *F.*, frontal; *Pef.*, prefrontal; *Pof.*, postfrontal; *Pob.*, postorbital; *P.*, parietal; *Sm.*, supramastoid; *St.*, supratemporal; *Int.*, intercalare; *So.*, supraoccipital; *Bo.*, basioccipital; Q., quadrate; *Pg.*, pterygoid; *Stap.*, Stapes.

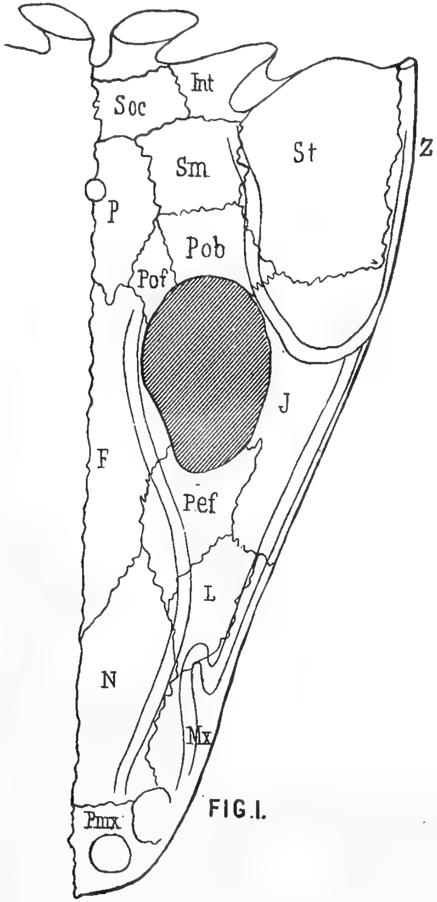


FIG. 1.

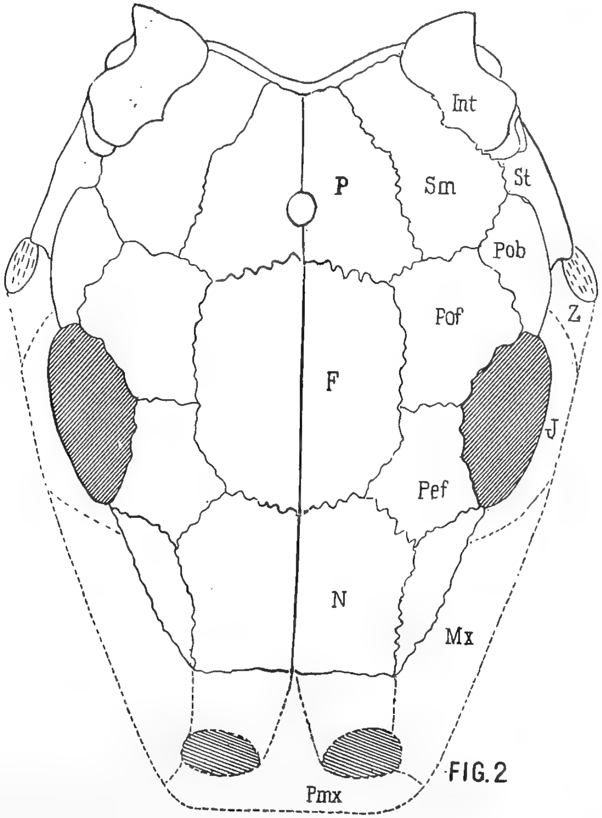


FIG. 2

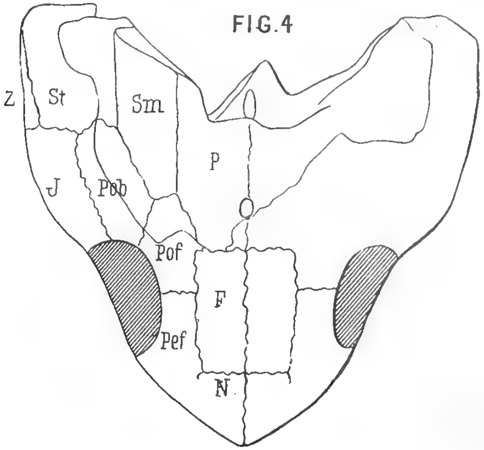


FIG. 4

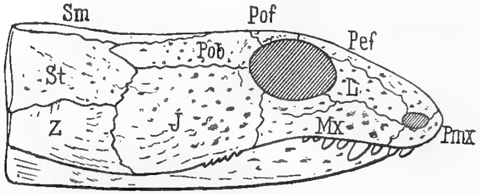


FIG. 4A.

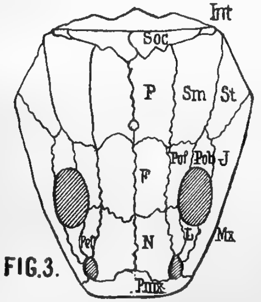


FIG. 3.

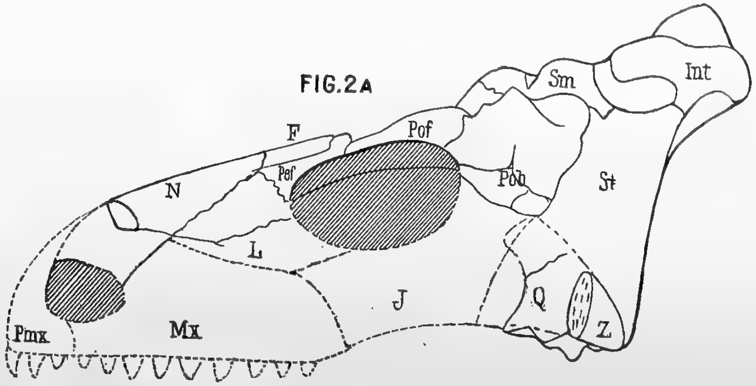


FIG. 2A

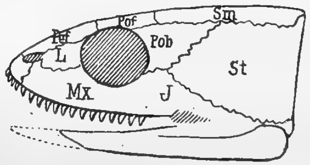
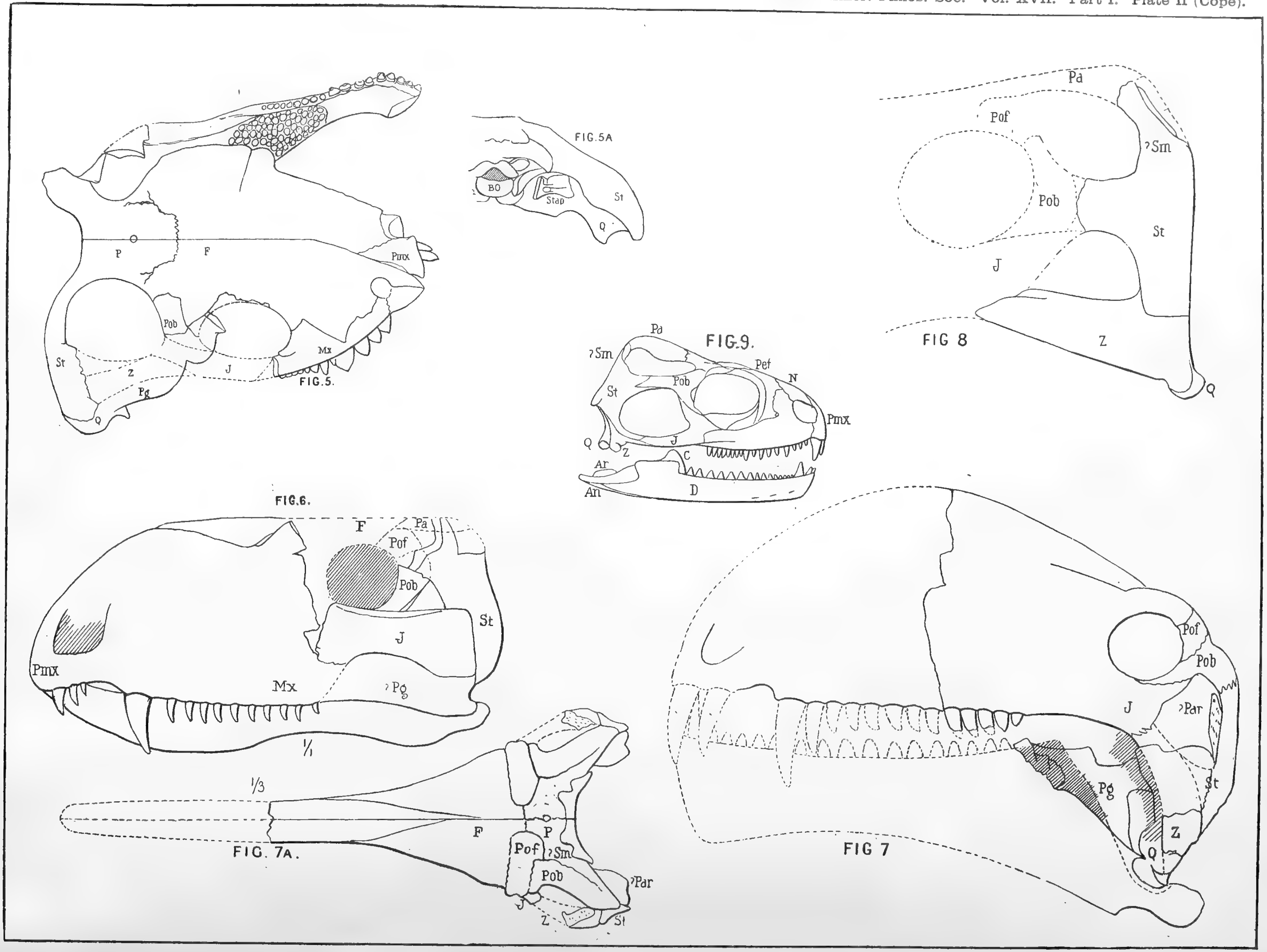
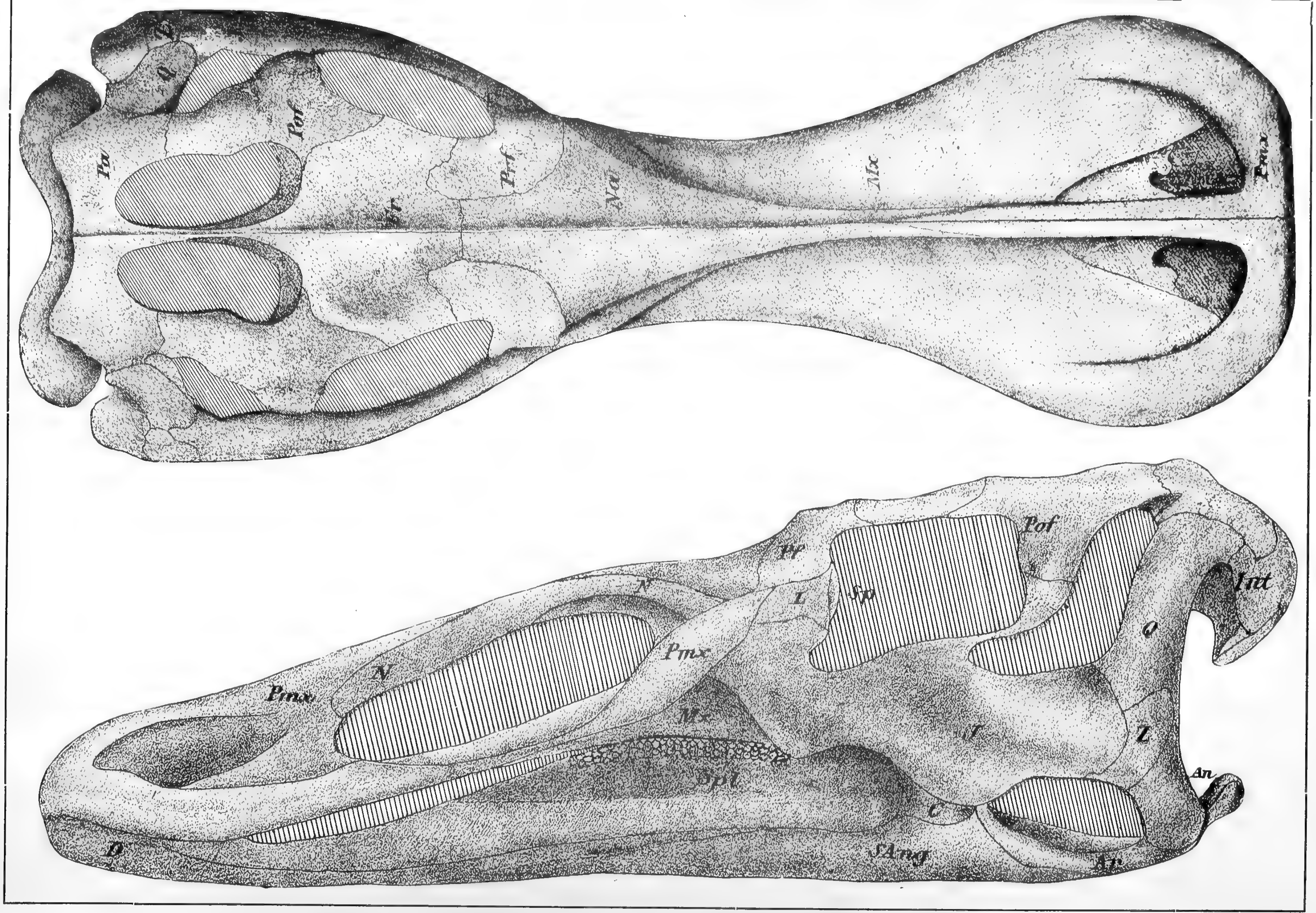


FIG. 3A.

1, Mastodonsaurus. 2, Chilonyx. 3, Pariotichus. 4, Pantylus.



5, Edaphosaurus. 6, Clepsydrops. 7, Naosaurus. 8, Diopeus. 9, Sphenodon.



Diclonius mirabilis.

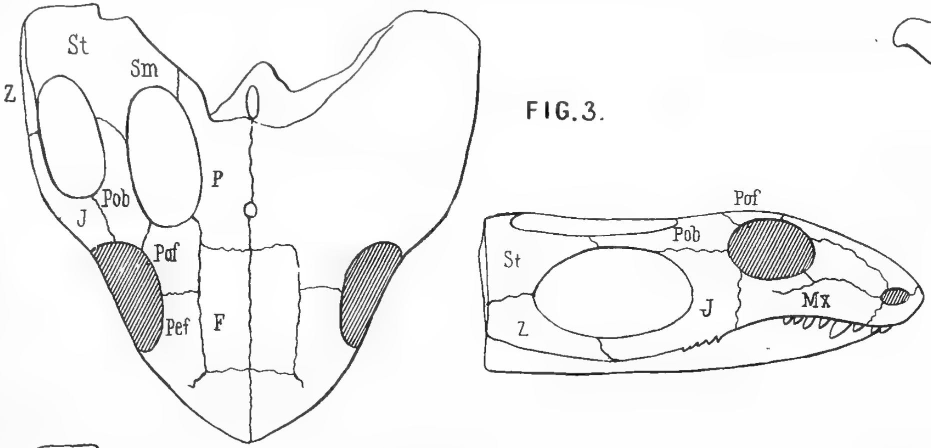


FIG. 3.

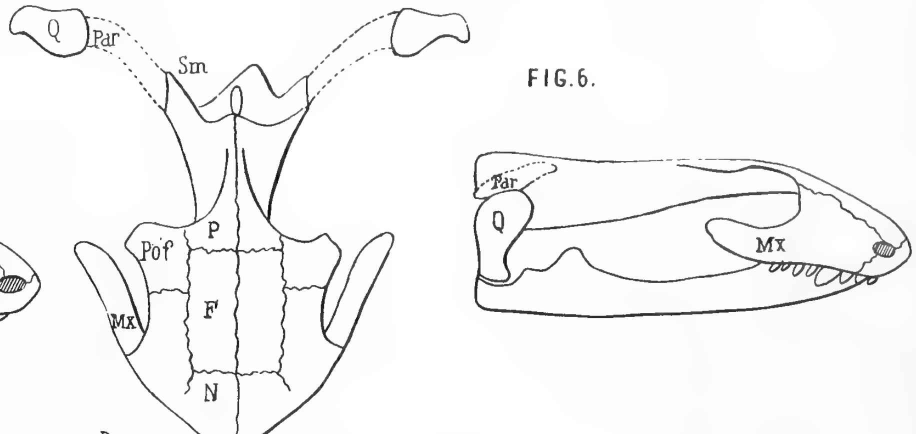


FIG. 6.

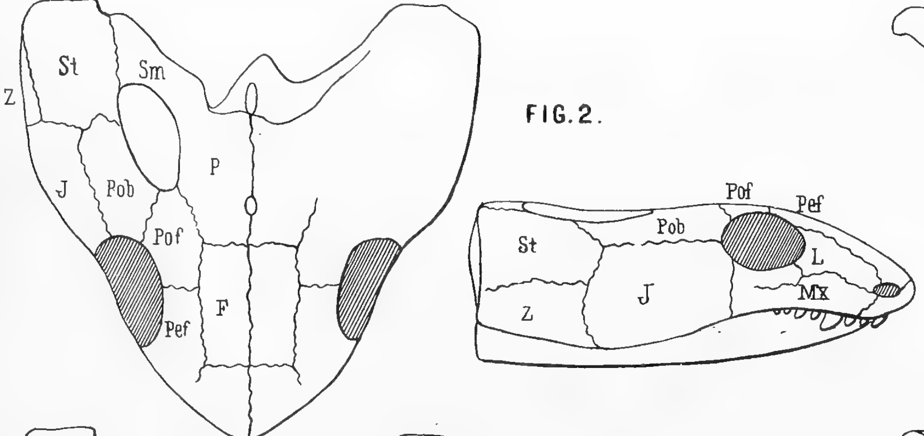


FIG. 2.

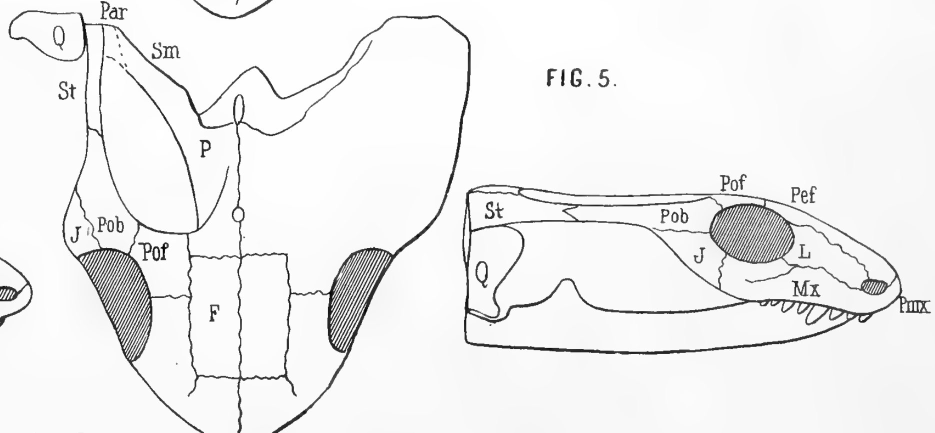


FIG. 5.

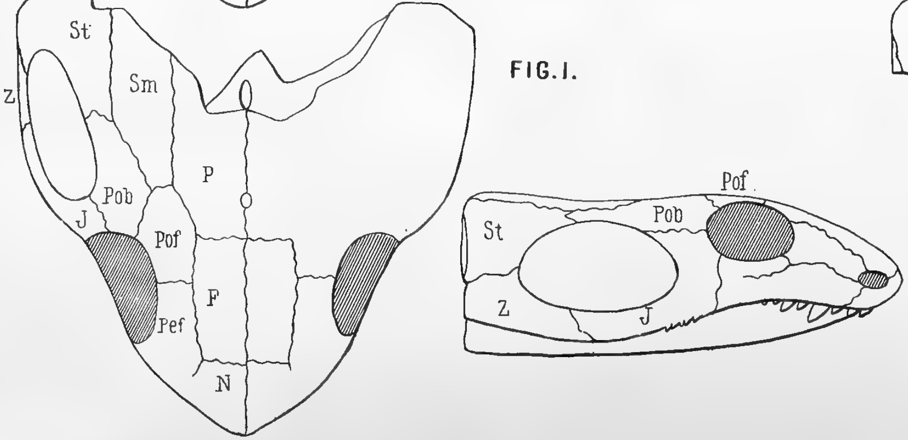


FIG. 1.

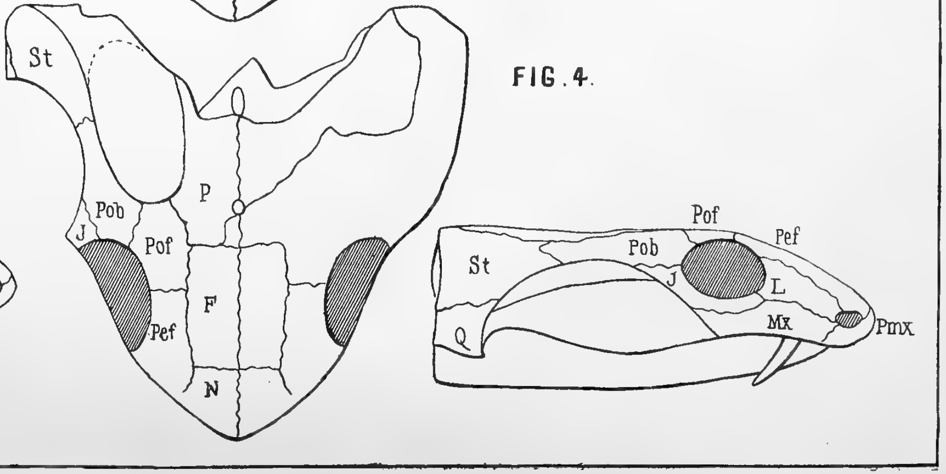


FIG. 4.

Types of Reptilia,

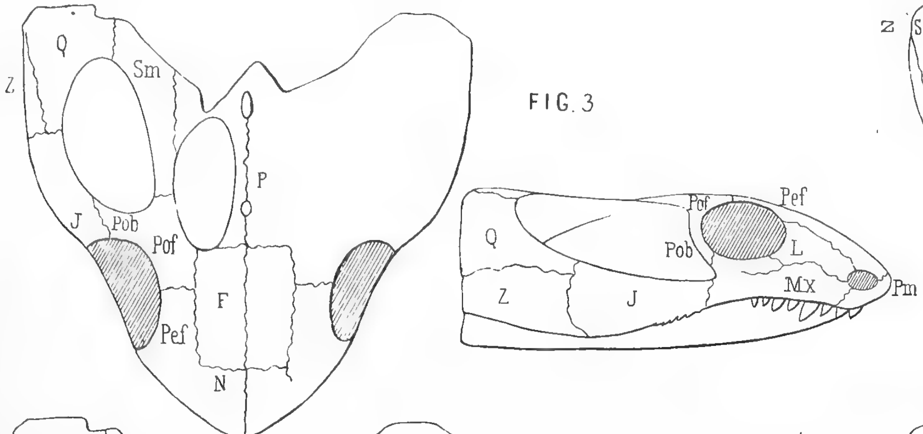


FIG. 3

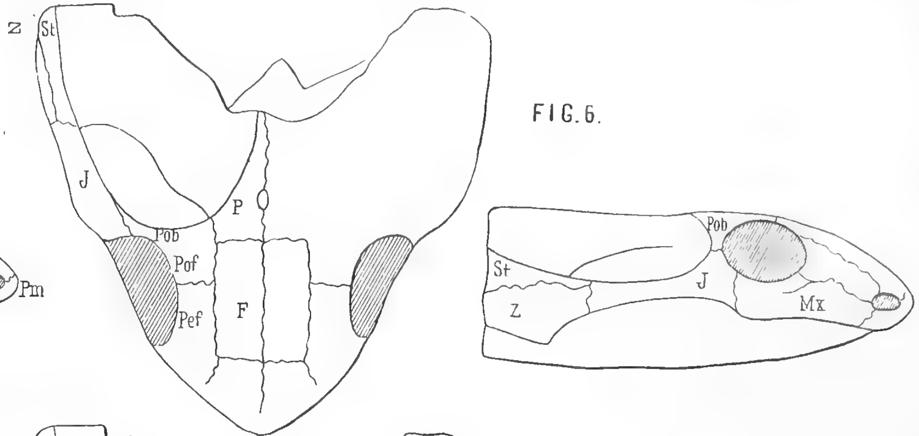


FIG. 6.

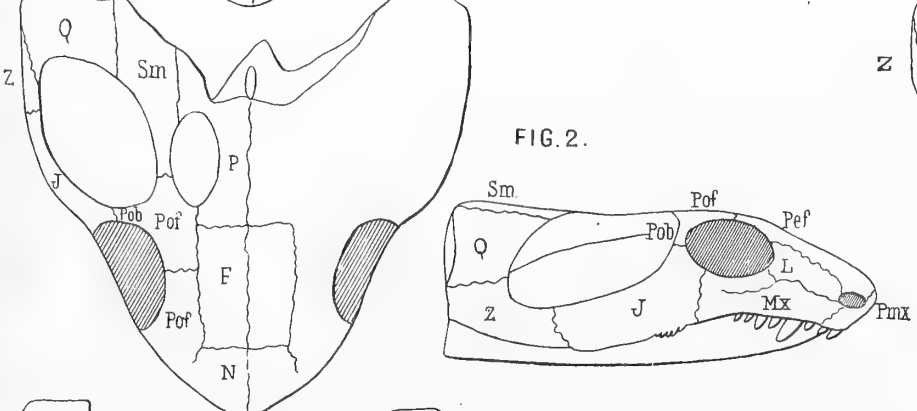


FIG. 2.

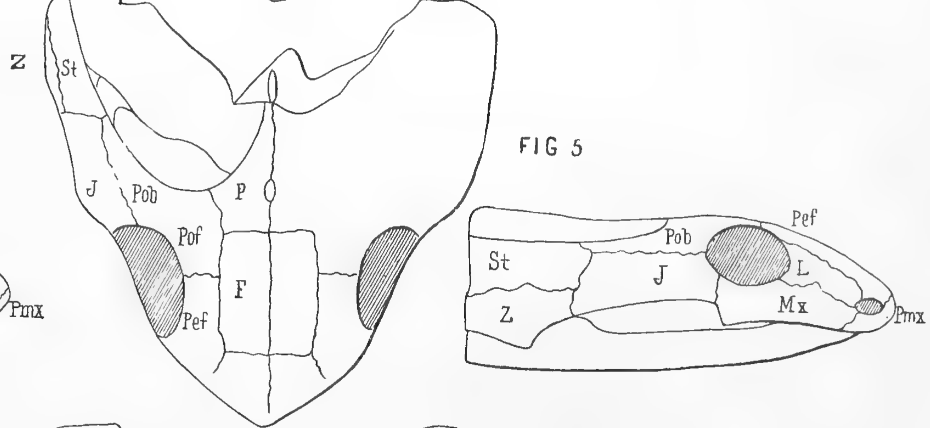


FIG 5

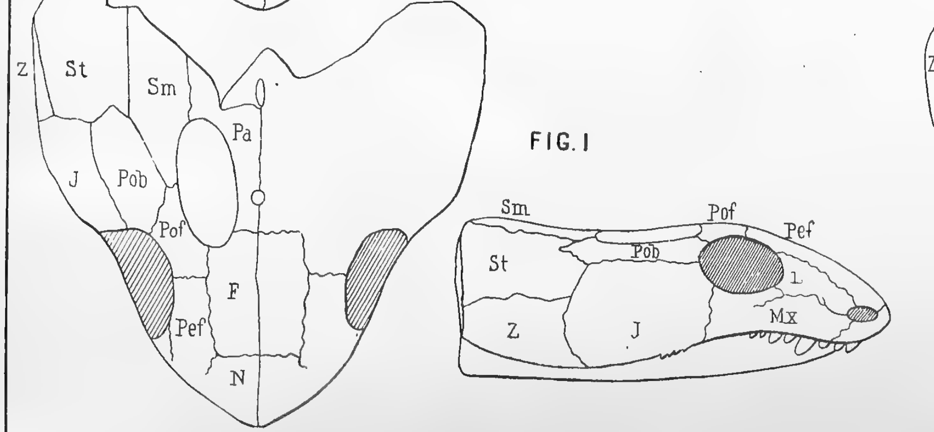


FIG. I

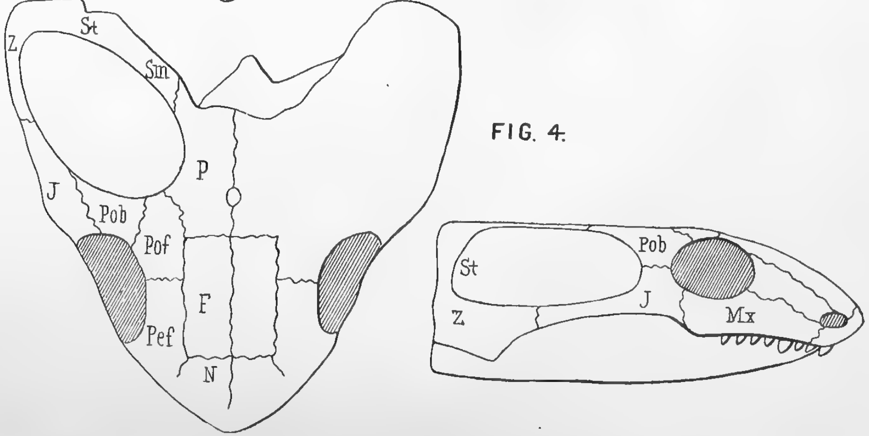


FIG. 4.

Types of Reptilia.

# ARTICLE III.

## A SYNOPSIS OF THE SPECIES OF THE TEÏD GENUS CNEMIDOPHORUS.

BY E. D. COPE.

**Read before the American Philosophical Society, January [illegible]1, 1892.**

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### CNEMIDOPHORUS Wagler.

Natur. Syst. Amphib., 1830, p. 154 partim; Wiegmann, Herp. Mexic., 1834, 9; Dum. Bibr., Erp. Gen., V, 1839, 123; Gray, Catal. Liz. Brit. Mus., 1 Ed., 1845, 20; Boulenger, 2 Ed., II, 1885, 360.

Scaly portion of tongue cordate behind, and non-retractile. Tail rounded. Teeth longitudinally compressed. Head large, regular; ventrals large; frontoparietals and parietals distinct. A collar-fold and femoral pores.

This genus embraces many species of the Neotropical realm, exclusive of the West Indian region, where it is replaced by Amiva.* Five species enter the Nearctic realm, and all but one of these are restricted to the Sonoran region. The *C. sexlineatus* Linn. ranges the entire Nearctic excepting the Hudsonian and Alleghenian districts, and the northern parts of the Central and Californian. The following are the characters of the species:

I. Nostril between the nasal plates. Males with a spine on each side the preanal region.

*A*. 10–12 longitudinal rows of ventral plates.

Brachial shields small, no post-antebrachials; 5 parietals; 4 supraoculars; femoral pores 29–35; olive, white-spotted........................................................ *C. murinus.*

*AA*. Ventral plates in 8 longitudinal rows.

Large brachials; no post-antebrachials; 5 parietals; 4 supraoculars; femoral pores 19; olive above with a lighter dark-edged dorsal band.................................... *C. espeutii.*

Large brachials; no post-antebrachials; 5 parietals; 4 supraorbitals; femoral pores 18–24; olive with 5–9 light longitudinal stripes ........................................... *C. lemniscatus.*

Brachials very small; black or blackish-brown with lines on the nape and spots on the outer side of the limbs ............................................................ *C. nigricolor.*

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*Dr. Steindachner describes (Annalen des K. K. Natur. Hofmus., Wien, 1891, p. 374) three species as *Cnemidophorus centropyx, tumbesanus* and *peruanus*, with large keeled dorsal scales. The last two have but one frontoparietal plate as in Dicrodon and Verticaria, and all three have the other external characters of those genera. The characters of the teeth are not mentioned.

II. Nostril anterior to nasal suture.

1. Ventral plates in 10–12 longitudinal rows.

Dorsal scales granular; edge of collar granular; brachials large; no post-antebrachials; femoral pores 10–12; 3 parietals; 3–4 supraorbitals; olive with rows of black spots, and 1 or 2 white lines on each side.......................................................... *C. lacertoides.*

Dorsal scales coarse, flat; scales of collar very small; parietals 3; supraoculars 4; brachials large; olive with nine longitudinal lines above............................. *C. longicaudus.*

2. Ventral plates in 8 longitudinal rows.

*A.* Scales of collar not larger at edge, which is more or less granular; supraorbitals 3 (parietals 3; no post-antebrachials).

Hind leg shorter, reaching meatus auditorius; anal scales continuous with abdominals; femoral scales in 6–7 rows; brachials larger; anals 10–12; usually five stripes on each side, *C. deppei.*

Hind leg longer, reaching nasal suture; minute scales between abdominals and anals; femoral scales in 10–12 rows; brachials smaller; anals 10–12; only four stripes on each side, *C. guttatus.*

*AA.* Scales of collar not larger at edge, which is more or less granular; supraorbitals 4 (parietals 3).

*a.* Prenasal not reaching second superior labial.

*β.* Post-antebrachial plates wanting.

Large; anal plates 10 or more; brachials in 4–5 rows; femoral pores 24–5; hind leg extended reaches ear; stripes broad and irregular....................................... *C. maximus.*

Medium; anal plates 5–6; brachials in 4–8 rows; femorals in 6–9; femoral pores 19–21; scales generally coarse; the hind leg extended reaches ear; stripes complete or broken up, *C. tessellatus.*

Smaller; anal plates 8–10; brachials 6 rows; femorals 8; femoral pores 25; hind leg extended reaches prenasal plate; yellow spotted on olive ground...................... *C. variolosus.*

Small; brachial plates 5 rows; femorals 6; femoral pores 17; scales smooth; striped; hind leg to ear................................................................ *C. octolineatus.*

Small; brachial rows 6; femorals 4–5; femoral pores 17; scales rough; unicolor; hind leg to ear................................................................... *C. inornatus.*

*AAA.* Collar with large scales, the largest at the edge.

*a.* Anterior nasal plate not reaching second superior labial.

*β.* Femoral pores 15 or more.

*γγ.* No post-antebrachial plates.

Small; stripes persistent, no intermediate spots; femur with a stripe behind; femoral pores 15–17; head short, loreal plate higher than long; femoral scales 7–8 rows; 5 infralabials, *C. sexlineatus.*

Large; stripes more or less connected with spots which cut up the dark ground into spots and crossbars posteriorly; femur without stripe behind; femoral pores 20–21; loreal plate longer than high; femoral scales 7–8 rows.......................................... *C. grahamii.*

*γγ.* Post-antebrachial scales present.

Median gular scales smaller than those of collar; femoral pores 16–18; femoral scales in 8 rows; infralabials 6; 7 undulate black stripes on an olivaceous ground .......... *C. septemvittatus.*

Median gular scales smaller than those of collar; femoral pores 18–23; muzzle elongate, loreal longer than high; dark bands interrupted by larger or smaller light spots or intervals, *C. gularis.*

*ββ.* Femoral pores fewer than 15.

Femoral pores 12 ; 3 parietals ; 3 supraorbitals ; gray brown with 10 longitudinal stripes, *C. multilineatus.*

Femoral pores 9-11 ; 5 parietals ; 4 supraoculars ; anals forming a triangle ; olive brown with 6 stripes or some rows of spots.................................................*C. ocellifer.*

*aa.* Anterior nasal plate reaching second labial.

Femoral pores 13 ; one marginal anal plate ; 6 white stripes ; small..................*C. labialis.*

In this genus as in others, some characters which are constant in one species are inconstant in another. The presence or absence of the sixth infralabial, and of the frenoörbital plates, are of this nature. The number of femoral pores varies within a small range in all of the forms. Anomalies in the division of the head plates are rare, but sometimes occur in this genus. Such are the fusion of the symphyseal and postsymphyseal plates, the presence of an additional labial plate, etc.

The discrimination of the North American species of this genus is the most difficult problem in our herpetology. Nowhere are subspecies more clearly defined than in Cnemidophorus, *i. e.*, definable geographical forms, which are not always true to their characters.

The color markings differ in the same individual at different ages, and the age at which the adult coloration is assumed differs in different localities. Some of the species, *e. g.*, *Cnemidophorus sexlineatus*, never abandon the coloration of the young of other species and subspecies. The same condition is characteristic of the *C. deppei* of Mexico, the *C. lemniscatus* of Brazil, and other species. The process of color modification is, as I have pointed out,* as follows: The young are longitudinally striped with from two to four stripes on each side of the middle line. With increasing age, light spots appear between the stripes in the dark interspaces. In a later stage these spots increase in transverse diameter, breaking up the dark bands into spots. In some of the forms these dark spots extend themselves transversely and unite with each other forming black cross-stripes of greater or less length. Thus we have before us the process by which a longitudinally striped coloration is transformed into a transversely striped one.

The large number of specimens of the *C. tessellatus* and *C. gularis* in the National Museum collection show that the breaking up of the striped coloration appears first at the posterior part of the dorsal region (*i. e.*, the sacral and lumbar). The confluence of the spots appears there first; and finally (*C. gularis semifasciatus*), where the color markings disappear, leaving a uniform hue, this also appears first at the posterior part of the body. In the *C. tessellatus rubidus* the dark spots disappear first on the anterior regions.

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* Proceeds. Amer. Philos. Soc., 1885, p. 283.

The species of Cnemidophorus inhabit dry open ground where they can observe their insect prey, and watch their enemies. From the latter they escape by the extreme rapidity of their movements, which renders it difficult to follow them with the eye, to which they appear as a streak flying over the ground. For this reason they are popularly known as "swifts." They are nevertheless frequently caught and eaten by snakes.

### CNEMIDOPHORUS MURINUS Laur.

Gray, Catal. B. M., p. 21; Dum. Bibr., Erp. Gen., V, 126 ; Bocourt, Miss. Sci. Mex. Rept., Pl. XX, Fig. 1; Boulenger, Catal. Liz. B. M., III, 361, *Leps murinus* Laurenti.

Guiana, Curaçoa, Trinidad.

### CNEMIDOPHORUS ESPEUTII Boulenger.

Catal. Liz. B. M., III, 362, Pl. XIX.

Old Providence Id.; Swan Id.; both off the east coast of Central America.

### CNEMIDOPHORUS LEMNISCATUS Daudin.

Gray, Catal. Liz. B. M., 21; Dum. Bibr., Erp. Gen., V, 128; Bocourt, Miss. Sci. Mex. Rept., Pl. XXc, Fig. 2; Boulenger, Catal. Liz. B. M., III, 363.

Tropical South America east of the Andes.

### CNEMIDOPHORUS NIGRICOLOR Peters.

Sitzber. Gess. Nat. Fr. Berlin, 1873, 76; Bocourt, Miss. Sci. Mex., Pl. XXc, Fig. 3; Boulenger, Catal. Liz. B. M., 364.

Los Roques Ids. off La Guayra, New Granada. (Known only to me by descriptions.)

### CNEMIDOPHORUS LACERTOIDES Dum. Bibr.

Erp. Gen., V, 134; Bocourt, Miss. Sci. Mex. Rept., XXc, Fig. 10; Boulenger, Catal. B. M., III, 373.

Southern Brazil, Uruguay, Argentine.

### CNEMIDOPHORUS LONGICAUDUS Bell.

Gray, Catal. Liz. Brit. Mus., 21; Bocourt, Miss. Sci. Mex. Rept., Pl. XXc, Fig. 13; Boulenger, Catal. Liz. Brit. Mus., III, 374.

*Amiva longicauda* Bell, Zool. Beagle Rept., 28, Pl. XV, Fig. 1.

Northern Patagonia.

### CNEMIDOPHORUS DEPPEI Wiegmann.

Herpet. Mexicana, 1834, p. 28; Bocourt, Miss. Sci. Mex. Rept., p. 281, Pl. XX, Fig. 3; Boulenger, Catal. Liz. B. M., 1885, 371.

There are three well-marked subspecies of the *C. deppei*, which differ in their coloration, and in the number of their femoral pores, and which have distinct geographical ranges. They are defined as follows:

Four with or without a median, or five narrow stripes on each side; sides green, unspotted; belly yellowish to black; hind legs with large spots; femoral pores 17–19...... *C. d. deppei.*

Five lateral and a vertebral stripe ; the lowest lateral a row of yellow spots on a green ground ; belly black ; legs scarcely yellow spotted ; femoral pores 21–23 ......... *C. d. decemlineatus.*

Five lateral and a vertebral stripe ; the lowest wide, and on the black sides, which have yellow spots below the stripe, often defining vertical black bars ; belly yellowish ; legs little spotted ; femoral pores 14–16 ................................................ *C. d. lineatissimus.*

### *Cnemidophorus deppei deppei* Wiegm.

*L. c.* Bocourt, *l. c. C. lattivitis* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 94.

One specimen from Guatemala, *Van Patten,* and two from Tehuantepec, *Sumichrast.*

### *Cnemidophorus deppei decemlineatus* Hallowell.

*Cnemidophorus decemlineatus* Hallowell, Proceeds. Academy Phila., 1860, 482.

Three specimens from Central America and twelve from Nicaragua, *C. Wright.*

The largest form, and distinguished by its color and numerous femoral pores.

### *Cnemidophorus deppei lineatissimus* Cope.

*Cnemidophorus lineatissimus* Cope, Proceeds. Amer. Philos. Soc., 1877, 94.

Sixteen specimens from Colima, Mex., *Xantus,* and four from Guadalaxara, *Major.*

This form is the most distinct in color characters, which are perfectly constant, and it is further characterized by the small number of femoral pores. It would rank as a species if compared with *C. d. decemlineatus* only, varying from the type in the opposite direction from that form.

### CNEMIDOPHORUS GUTTATUS Wiegm.

Herp. Mexicana, 1834, 29 ; Bocourt, Miss. Sci. Mex. Rept., 285, Pl. XXc, Fig. 4; Boulenger, Catal. Liz. Brit. Mus., 1885, II, 370.

This species presents several forms which may be regarded as subspecies until their constancy can be proven. They differ as follows :

I. Brachial and postbrachial plates continuous ; few or no granules on the edge of the collar.

Four light stripes on each side ; large ...................................... *C. g. immutabilis.*

II. Brachial and postbrachial plates separated by smaller scales ; numerous granules on edge of collar.

Four light stripes on each side ; small ; back not spotted .................. *C. g. microlepidopus.*

Two light stripes on each side ; the back light spotted ; large .................... *C. g. guttatus.*

Unicolor ; small ......................................................... *C. g. unicolor.*

### *Cnemidophorus guttatus immutabilis* Cope.

*Cnemidophorus immutabilis* Cope, Proceeds. Amer. Philos. Soc., 1877, 93.

This form might be regarded as a species but for the fact that its characters are not entirely trustworthy. Thus one of the specimens has a few granules at the middle of the edge of the collar, and there are a few smaller scales between the large brachial and postbrachial scales.

Two specimens from Tehuantepec, *Sumichrast*, the larger equal in size to the *Amiva surinamensis*.

### *Cnemidophorus guttatus microlepidopus* Cope.

*Cnemidophorus microlepidopus* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 370.

This form differs from the typical *guttatus* in color only, and may be the young. The median dorsal region is, however, unspotted.

One specimen, Tehuantepec, *Sumichrast*.

### *Cnemidophorus guttatus unicolor* Cope.

*Cnemidophorus unicolor* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 93.

The form is represented by one of the smallest specimens. According to the rule which prevails in this genus, it should be striped if merely the young of the *C. g. guttatus*. The absence of stripes then indicates probably a race different from the typical form of the species.

One specimen from Tehuantepec, *Sumichrast*.

### *Cnemidophorus guttatus guttatus* Wiegm.

*Cnemidophorus guttatus* Wiegm., *l. c.;* Bocourt, *l. c.;* Boulenger, *l. c.*
*Amiva guttata* Cope, Proceeds. Acad. Phila., 1862, p. 63.

Three specimens from Jalapa, *Pease*, in the Museum of the Philadelphia Academy.

The above specimens are of relatively large size, equaling the *C. g. immutabilis*.

### CNEMIDOPHORUS MAXIMUS Cope.

Proceeds. Academy Phila., 1863, p. 104.

The largest species of the genus, equaling many of the Amivas in dimensions. It inhabits the peninsula of Lower California.

This species varies in the number of its anal plates, some specimens having fewer than others. The brachial plates also vary in number from six to eight rows. Two young specimens (No. 12,658) in which the umbilical fissure is still open, are about as large as the adult *C. sexlineatus*. They have a median dorsal light stripe, and two on each side on a blackish ground. Each of the two dark bands thus produced is marked by two rows of pale spots. In this they differ from the spotted striped form of the *C. tessellatus* and *C. sexlineatus*, which have but one series of such spots. The femur and tibia are crossbarred, and the former is not marked with a longitudinal stripe behind.

## CNEMIDOPHORUS TESSELLATUS Say.

Baird, U. S. Pac. R. R. Surveys, Vol. X, 1859, Gunnison's Report, p. 18.
Cope, Check List Batr. Rept. N. Amer., 1875, 46.
*Amiva tessellata* Say, in Longs. Exped. Rocky Mts., 1823, II, p. 50.

Scales of the back and sides generally coarse, .05 mm. in diameter. Scales of the collar not larger than those of the throat, the edge of the collar with smaller often granular scales. Four supraorbital scales, the posterior smaller than the others. These are separated from both the superciliaries and the frontal and frontoparietal by granular scales whose extension anteriorly differs in different individuals. Frontoparietals as large as the parietals, truncate in front. Interparietal longer than broad, longer than each parietal. The latter undivided. A transverse series of small plates bound the parietals and interparietals posteriorly. Frenal plate longer than postnasal. One row of scuta in front of orbit, and below orbit, separating the latter from the superior labials. Superior labials five to below middle of orbit, the fifth acuminate posteriorly. Infralabials five.

Brachial scales in four to eight longitudinal rows (rarely five) counted at the middle, continuous with antebrachials, which are in three rows (rarely two). Postantebrachials small, uniform. Femoral plates in seven to nine rows (counted at middle and to the line of pores) and tibial plates in three longitudinal rows. Femoral pores varying from nineteen to twenty-one in number.

Color varying from olivaceous black to olivaceous brown, which is marked by light yellow or orange longitudinal stripes or spots on the dark ground, or reversed by black spots on a light ground. The head is unspotted and unstriped, except occasional maculations of the gular region. Belly from yellowish to black or spotted. Limbs crossbarred or spotted, and not distinctly striped posteriorly.

The size varies from a length of head and body of 86 m. to 102 mm. In the former the total length is 260 mm.; in the latter, 350 mm. For more detailed measurements see under the respective subspecies.

This species ranges over the Sonoran and Lower Californian regions and the Pacific, nearly to the northern boundary of California. Its distribution is somewhat coincident with that of the *Eutænia elegans* (omitting the Rocky mountains proper), and its eastern border is overlapped by the range of the eastern *C. sexlineatus*. The range of variations of color seen in the *C. tessellatus* is about the same as that seen in the *C. gularis*, although, with a few exceptions, the subspecies of the two may be distinguished from each other by color characteristics, without examining the scale characters. The parallelism is, however, very close, and shows the same line of modifications. I refer more especially to these under the head of *C. gularis.*

The subspecies of the *C. tessellatus* are five, as follows:

I. Brachial scales 4–5 rows; femorals 6–7 rows.

Blackish olive above with a median dorsal paler stripe, and three similar stripes on each side; belly and throat unspotted .......... *C. t. perplexus.*

Two pale stripes on each side only, the interspaces pale spotted, and frequently broken up into black or olive spots so as to destroy their integrity; generally sparsely black spotted below, *C. t. tessellatus.*

No stripes, but 12–14 longitudinal series of pale spots on an olivaceous ground, more or less confluent; hind legs with numerous pale spots; thorax, collar, and more or less of throat, black .......... *C. t. melanostethus.*

II. Brachial scales in 5–6 rows; femorals 8–9 rows.

No stripes; ground color dove brown, with 3 rows of more or less obsolete black spots on the back, and vertical black bars on the sides; abdominal plates pale, black edged; hands and inferior faces of hind legs and tail red; larger .......... *C. t. rubidus.*

III. Brachial scales 7–8 rows; femorals in 8–9 rows.

Four light stripes above, interrupted and connected with light spots and lines in the black interspaces, sides, throat and inferior surfaces variegated black and white; medium, *C. t. multiscutatus.*

## *Cnemidophorus tessellatus perplexus* Bd. Gird.

*Cnemidophorus perplexus* Bd. Gird., Proceeds. Acad. Phila , 1852, p. 128.
Cope, Check List Batr. Rept. N. Amer., 1875, p. 46.

The type specimen is the largest obtained, and is probably adult. Its colors are rather obsolete, while those of three younger specimens are as strongly contrasted as in the young of any other form. Among all the striped forms of the *C. tessellatus*, this one is distinguished by the presence of seven stripes and no spots. It is, so far as yet known, confined to the valley of the Rio Grande river.

## *Cnemidophorus tessellatus tessellatus* Say.

*Cnemidophorus tessellatus* Baird, *l. sup. cit.*; Cope, *l. sup. cit.*; *Amiva tessellata* Say, *l. sup. cit.*
*Cnemidophorus gracilis* Bd. Gird., Proceeds. Acad. Phila., 1852, 128; Baird, U. S. Mex. Bound. Surv., Report II, Pt. II, Rept., p. 10, Pl. XXXIV, Figs. 7–14.
*Cnemidophorus marmoratus* B. & G., Proceeds. Acad. Phila., 1852, p. 128.
*Cnemidophorus tigris* Bd. Gird., Proceeds. Acad. Phila., VI, 1852 (April), 69; Baird, U. S. Mex. Bound. Surv. Rept., 1859, II, Pt. II, Reptiles, p. 10, Pl. XXXIII.
*Cnemidophorus tessellatus tigris* Cope, Check List Batr. Rept. N. Amer., 1875, p. 46.
*Cnemidophorus undulatus* Hallow., Proc. Acad. Phila., VII, 1854, June, p. 94

The adult differs from the young in color, and its colors may be best understood by reference to the latter. In this stage the ground color of the back and sides is black or blackish olive, and it is transversed by two light yellowish stripes on each side. One of these starts at the occipital plate, and the other at the superciliary angle. The lateral stripe which extends from above the auricular meatus in the *C. t. perplexus* is here wanting. There is sometimes a trace of a median dorsal stripe, but generally not. Faint longitudinal lines are sometimes present between the stripes mentioned. On the sides below the external stripe are three series of more or less longitudinal spots, which outline three stripes; but they are not connected, excepting sometimes in the transverse direction. This stage represents the *C. gracilis* B. & G.

In mature specimens rounded spots appear between the longitudinal stripes, and the lateral spots become connected transversely so as to leave the dark ground color in the form of irregular transverse bars (Nos. 3047, 4970 and 15,619). In some specimens the median dorsal stripe is distinct, and is even divided into two (No. 11,978). Such specimens have six stripes very close together, but only the external pair on each side are homologues of those of the *C. sexlineatus* and *C. gularis.* In the majority of adult specimens the light spots expand transversely and produce an emargination on one side or the other of the black ground, or cut it into sections or spots, by expanding in both directions. In the former case the dark stripes become irregular or undulate in outline. This is the usual condition on the anterior part of the body. On the posterior part of the body the dark ground is usually broken into spots. In the type specimen of the *C. tigris* B. & G. the breaking up of the black intervals had not been completed, although the specimen is of full size. In typical specimens this part of the body is marked by three longitudinal rows of transverse black spots. The upper surface of the tail is generally marked with brown spots, sometimes rather large, but in other specimens confined to the keels of the scales. In some they are wanting.

In the last modification the traces of stripes have almost or quite disappeared. The upper pair are first to be interrupted by transverse and oblique extensions of the irregularly shaped black spots, and the inferior stripes are finally interrupted and lost in the same manner. Thus in Nos. 8633 and 3048*a*, the spots are transversely confluent in every direction, bearing only irregular areas of the white color, now become the ground. These approach nearest to the *C. variolosus* m., and represent the *C. marmoratus* of Baird and Girard. In the type of that supposed species a trace of the inferior stripe remains on each side. The end of the fourth toe of the extended posterior foot reaches the *meatus auditorius*, and there are twenty femoral pores on each side. The length of the head and body is 85 mm.; in No. 8633 it is 100 mm.

Hallowell, in describing this subspecies as *C. undulatus*, recognized the difference between it and the *C. t. perplexus*, remarking that the present form has but two light stripes on each side.

This form ranges the Sonoran and Lower Californian regions to Utah, inclusive, and extends to the northern part of California.

### *Cnemidophorus tessellatus melanostethus* Cope.

Check List Batr. Rept. N. Amer., 1875, p. 46.
*Cnemidophorus melanostethus* Cope, Proceeds. Acad. Phila., 1863, p. 104.

The coloration of this subspecies is something like that of the *C. variolosus*, but that is another species. The interparietal plate is narrower than in the *C. t. tessellatus*, and the black breast and gular region are not seen in it.

A number of young specimens accompany the two adults described. They have two narrow stripes on each side of the middle line, and the spaces between them contain each a row of pale spots. The thorax is not black. These resemble the young of *C. t. tessellatus* (*C. gracilis*), but the latter has brighter colors, and where the spaces between the stripes contain marks there are delicate longitudinal lines (No. 3034, type of *C. gracilis*).

This form is only known from the Colorado river of Arizona.

A form very much like this subspecies has been named *C. martyris* by Stejneger.* The two known specimens differ from the *C. t. melanostethus* in their smaller size and in the extension of the black over the entire inferior surface. It is doubtful whether it can be regarded as a subspecies. It is from the Island of San Martir, Gulf of California.

### *Cnemidophorus tessellatus rubidus* Cope.

This elegant form is represented in the National collection by seven individuals, of which three are adult. To the usual characters of the species it adds some others. Thus the scales are rather finer, being less than .5 mm. in diameter. The femoral scales are more numerous. Femoral pores twenty-two. Small scales of collar border not granular.

There are three parietals, and the longest toe reaches the auricular meatus. There are the usual three anals, with one in front of the median, which is, with the latter, bounded by a few scales on the sides. Median gular scales rather coarse.

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* Proceeds. U. S. Nat. Museum, XIV, 1890, p. 407.

Loreal longer than high. Small scales above anterior canthus of eye numerous and rather prominent. The keels of the caudal scales are prominent, and except at the base of the tail, in continuous lines.

The color of the upper surfaces in the adult is a dove brown. This is marked on the back by three series of transverse black spots, which are well separated from each other. In one specimen the spots are very narrow; in another they are nearly obsolete on the anterior part of the back. On the sides similar black spots are more or less confluent into vertical black stripes. The head and fore legs are uniform brown above; the hind limbs have on a similar ground narrow blackish crossbars, sometimes indistinct. Tail pale brown above with olive and brown spots. Inferior surfaces straw colored tinged with green, and varied with black and red. The abdominal scuta are black bordered, and the throat is black spotted, sometimes strongly, sometimes faintly. The palms and sometimes the entire inferior surface of the anus is a bright vermilion. Posterior and inferior sides of femora, inferior aspect of tibia, and inferior side and distal half of tail bright vermilion.

The young specimens have traces of six longitudinal stripes of an olivaceous or light brown color, and the spaces between them are crossbarred with black and olive, as in the *C. gularis mariarum*, which this form closely resembles at this stage. The black spots become more distinct with age, and the interspaces blend completely with the stripes, so that the latter are ultimately completely lost in a common ground color. The femora are reticulated with black on an orange ground above. The black and red of the inferior surfaces are not so pronounced as in the adult.

| *Measurements.* | *M.* |
|---|---|
| Total length | .340 |
| Length to posterior edge of ear | .024 |
| Length to collar | .034 |
| Length to vent | .100 |
| Length of fore limb | .035 |
| Length of hind limb | .072 |
| Length of hind foot | .036 |

*Cnemidophorus tessellatus rubidus* Cope.

| *Catalogue Number.* | *Number Specimens.* | *Locality.* | *Whence obtained.* |
|---|---|---|---|
| 15,149 | 1 | St. Margareta Id., Lower California. | U. S. Fish Commission Steamer *Albatross.* |
| 50 | 1 | | |
| 1 | 1 | | |
| 2 | 1 | | |
| 3 | 1 | | |
| 4 | 1 | | |
| 5 | 1 | | |

## *Cnemidophorus tessellatus multiscutatus* Cope.

*Cnemidophorus tessellatus tigris* B. & G., Cope, Proceeds. U. S. Nat. Museum, 1889, p. 147; not of Baird and Girard.

Represented in the U. S. National Museum by four specimens of medium size. The muzzle is rather acute, and moderately elongate. The extended hind leg reaches to the orbit. In two larger specimens there are six plates of the infralabial row, and in two smaller but five. Four large anals, two on the middle line in front of the marginal pair. These four are surrounded by a series of smaller plates as far as the vent. Scales of the tail with the keels slightly oblique throughout. The peculiarity of the subspecies is seen in the large number of rows of brachial scales (7–8 rows), and femoral scales (8–9 rows). The former are not quite constant, however, one of the smaller specimens having but six rows. Femoral pores 20–22. The scales are smaller than is usual in *C. tessellatus*, measuring .33 and .25 mm. in diameter.

The color is generally of the *C. tessellatus tessellatus* type, but the black ground color is more persistent. The light stripes are most broken up posteriorly, and the communicating pale cross-spots are widest and most numerous. On the sides the pale spots are of irregular shapes, being both longitudinal and transverse on a black ground. Belly black and light olive in varying proportions. Gular region and collar with transverse black spots or bands. Fore limbs black with light olive spots; hind limbs brown with blackish reticulation. Tail brown above, black-spotted below.

| *Measurements.* | *M.* |
|---|---|
| Total length | .275 |
| Length to meatus auditorius | .021 |
| Length to collar | .030 |
| Length to vent | .085 |
| Length of fore limb | .032 |
| Length of hind limb | .065 |
| Length of hind foot | .035 |

*Cnemidophorus tessellatus multiscutatus* Cope.

| *Catalogue Number.* | *Number Specimens.* | *Locality.* | *Whence derived.* |
|---|---|---|---|
| 15,160 | 1 | Cerros Island, west coast of Lower California. | U. S. Fish Commission Steamer *Albatross.* |
| 1 | 1 | | |
| 2 | 1 | | |
| 3 | 1 | | |

## CNEMIDOPHORUS VARIOLOSUS Cope.

This species exhibits the general scale characters of the *C. tessellatus*, but possesses some peculiarities. The interparietal plate is twice as large as either parietal. Infralabials five. The scales of the brachium and of the femur are smaller and more numerous than in the *C. tessellatus*. There are six rows of the former, four being the usual number in the latter species; and eight of the latter, six or seven being the usual number. Brachial rows three; tibials three. Anal scuta with the lateral scales rather larger than usual, giving four large and six small ones in all. Femoral pores more numerous, twenty-five on each side. This species is especially characterized by the length of the hind leg, which reaches, when extended, to the postnasal plate, instead of to the *meatus auditorius* only. The scales of the mesoptychium extend all the way across, and are not interrupted at the middle by smaller ones as in the *C. t. perplexus*. The marginal scales are smaller. Posterior gular scales are smaller, bounded in front by the larger scales of the anterior gular region.

Total length 250 mm.; of head and body to vent 65 mm.; of head to angle of mandible 10 mm.; to collar 24 mm.; to axilla 31 mm.; length of fore leg 27 mm.; of fore foot 12 mm.; of hind leg 55 mm.; of hind foot 30 mm.

The typical specimen is of a size which would be fully striped if it belonged to the *C. maximus* or *C. tessellatus*, being that of the eastern *C. sexlineatus*. There are, however, no stripes, but the olivaceous ground of the superior surfaces is marked with numerous rather small yellowish oval spots. Those of the sides are irregularly disposed, but those of the superior surfaces are arranged in six more or less irregular series. Of these the two external on each side correspond with the two external stripes of the young of the *C. tessellatus*. On the nape the series lose their regularity, and on the nape region they are more frequently transverse. The hind legs are olivaceous, marked with numerous irregular oval yellow spots. No stripe on the posterior face of the femur. Head without spots or stripes. Gular region dark olive; thorax blackish; belly yellowish, the scales with black bases. Tail olive with scales above yellowish at the base, brownish beyond; below brown except the basal fourth, which is yellowish with black spots on most of the scales. Posterior limbs with oval yellowish spots on an olivaceous ground. Femur not striped behind.

This species resembles the *C. maximus* in the increased number of its femoral pores and femoral and brachial scales, but is distinguished by its much longer hind leg, spotted coloration and much smaller size.

*Cnemidophorus variolosus* Cope.

| *Catalogue Number.* | *Number Specimens.* | *Locality.* | *Where obtained.* | *Nature of Specimen.* |
|---|---|---|---|---|
| 3066 | 1 | Parras Coahuila. | Lieut. Couch, U.S.A. | Alcoholic. |

### CNEMIDOPHORUS OCTOLINEATUS Baird.

Proceeds. Academy Phila., 1858, p. 255.
U. S. Mexic. Boundary Survey, II, 1859, Pt. II, Reptiles, p. 10.
Cope, Check List Batr. Rept. N. Amer., 1875, p. 45.

This species differs from the young specimens of the *C. tessellatus* of equal size, in the small number of its femoral pores, and in the absence of spots on the hind limbs and sides, as well as in the additional pair of median longitudinal stripes. The single known specimen is apparently adult, and is about equal in size to a half-grown *C. tessellatus*, and smaller than the *C. variolosus*.

### CNEMIDOPHORUS INORNATUS Baird.

Proceeds. Acad. Phila., 1858 (Dec.), 255.
Rept. U. S. Mex. Bound. Survey, II, 1859, Pt. II, Rept., p. 10.
Cope, Check List Batr. Rept. N. Amer., 1875, p. 45.

This species is distinguished by a combination of characters. The rough scales are peculiar to it, and it is the only species known to me in which the rows of brachial plates exceed the femoral in number. It is the smallest species, and yet shows no indication of stripes.

### CNEMIDOPHORUS SEPTEMVITTATUS Cope.

Scales of collar large, in three transverse rows, the largest row on the edge; scales of mesoptychium small, flat, those of gular region longer. Head narrower than in any other species, the first and second supraorbital plates longer than wide, the fourth well developed. Interparietal plate twice as long as wide, considerably narrower than the parietals; both bounded posteriorly by some small plates. Loreal much longer than postnasal; no frenoörbital. Infralabials six on each side, the first pair in contact throughout. Dorsal scales coarse, round, projecting upwards at their posterior border. Brachial scales in six rows, antebrachials in three. One row of very large post-antebrachials, bounded by smaller ones. Femorals in eight rows, tibials in three. Femoral pores 16–18. Anal plates only three, separated from vent by a wide granular space, and surrounded anteriorly and laterally by one row of small flat scales. Legs rather short, hind foot reaching to half way between humerus and auricular meatus.

Size above medium for the genus. Length of head and body to vent (tail injured) 110 mm.; length of head to angle of mandible, 26 mm.; do. to collar 34 mm.; do. to axilla 42 mm.; do. to fore leg 31 mm.; do. of fore foot 25 mm.; do. of posterior leg 71 mm.; do. of hind foot 35 mm.

Color above light olivaceous brown, transversed by seven longitudinal broad black stripes, three on each side and one on the middle line. On the lumbar region the median band disappears, and the pale intervals are wider than the black ones; anteriorly the pale ground assumes its normal relation of stripes on a black ground. The inferior commences at the orbit and passes over the tympanum; the next begins above the anterior border of the orbit and marks the external borders of the supraorbital plates. The next issues from a parietal plate. Anteriorly the black interspaces have a few small spots; posteriorly they become undulate through lateral emarginations, and more posteriorly the first and second stripes are broken up into quadrate spots, the third remaining unbroken. The hind legs are very indistinctly marbled on an olive-gray ground. The fore legs are coarsely reticulated with black on an olive ground. The lateral dark stripes extend to the orbit, and there is a blackish shade on the side of the muzzle, just below the canthus rostralis. Lower surfaces everywhere yellowish, unspotted, except a few black specks on the inferior labials and sides of the gular region. Tail olive above, yellowish below.

This species belongs to the *C. sexlineatus* series, as indicated by the scales of its collar, but it has the coarse scales of the *C. tessellatus*. Its six infralabial scales are found only in the former series. Its coloration resembles in some degree the stage of the *C. tessellatus tessellatus*, called by Baird and Girard *C. tigris*, but it has seven stripes instead of four, and the lateral stripes are broken up and not the median, as is the case in the latter. It also differs from the latter in the marking of the fore leg, and nearly uniform coloration of the hind leg; the reverse being the case in the *C. tessellatus*. The striping of the head is also not seen in the latter. The head is also narrower in proportion to its length.

This, perhaps the handsomest species of the genus, is represented in the collection by an adult female only. It represents the *C. sexlineatus* in California.

*Cnemidophorus septemvittatus* Cope.

| *Catalogue Number.* | *Number Specimens.* | *Locality.* | *Whence obtained.* | *Nature of Specimen.* |
|---|---|---|---|---|
| 2872 | 1 | El Dorado Co., Cal. | Dr. C. C. Boyle. | Alcoholic. |

### CNEMIDOPHORUS SEXLINEATUS Linn.

Gray, Catal. Brit. Mus. Liz., 18, p. 21.
Dum. Bibron, Erp. Gen., V, p. 131.
Cope, Check List Batr. Rept. N. Amer., 1875.
Bocourt, Miss. Sci. Mex. Rept., 273, Pl. XXc, 11.
Boulenger, Catal. B. M., II, 1855, 364.
*Lacerta sexlineata* Linn., S. N., I, p. 364.
*Amiva sexlineata* Holbrook, N. Amer. Herp., 63, Pl. VI; 2d Ed., II, 109, Pl. XV.

Scales of collar large, in few rows, the largest at the border, larger than the median gular scales. Scales of body minute, .033 mm. in diameter. Large gular scales with abrupt posterior border extending entirely across throat. Four supra-orbitals. Frontoparietals large as parietals, truncate in front. Interparietals narrower than parietal, parallelogrammic. Labial scales five to below orbit; infralabials five or six, the anterior pair in contact throughout. Brachial scales in six to eight rows; antibrachials in three; femorals in from six to eight. Femoral pores 15–17. Anal plates three large ones; two posterior, one anterior. Longest toe of extended hind leg reaching to meatus auditorius.

The young have six longitudinal light stripes on a dark ground, which persist in adults; the dark interspaces being never marked by light spaces as in the *C. gularis.* The limbs are pale spotted on a darker ground and there is a longitudinal light stripe on the posterior face of the femur.

This is one of the smallest species, and it retains the young coloration everywhere. It is also distinguished by its short and high muzzle, and the absence of postantebrachial scales. It covers the Austroriparian region of the Nearctic realm and the eastern as far as the range of the Carolinian district, extending to Maryland and Delaware, but not New Jersey. In the Central region it reaches north to the Sand Hills of the Loup Fork river of Nebraska. Its southwest limit is in Texas.

Two specimens from Florida (one of them from Key West, No. 15,336) display the anomaly of a fusion of the three large anal plates into one. All other Florida specimens are normal.

### CNEMIDOPHORUS GRAHAMII Bd. Gird.

Proceeds. Acad. Phila., 1852, p. 128.
Baird, U. S. Mexican Bound. Surv., II, 1859, p. 10, Pl. XXXII, Figs. 1–6.
Cope, Check List Batr. Rept. N. Amer., 1875, p. 45.

A distinct species which resembles in coloration the partly crossbanded forms of the *C. tessellatus-tessellatus.* But two specimens are known, and one of these has five and the other six infralabial plates. They are from Western Texas, between San Antonio and El Paso.

## CNEMIDOPHORUS GULARIS Bd. Gird.

Proceeds. Acad. Phila., 1852, p. 128.
Baird, U. S. Mex. Boundary Survey, Reptiles, Pl. XXXIV, Figs. 1–6.
*Cnemidophorus guttatus* Hallowell, Proceeds. Acad. Phila., 1854, p. 192.

This species is allied to the *C. sexlineatus*, but is distinguished by the presence of postantebrachial plates, the more numerous femoral pores and the longer muzzle. It is very variable as to size and color, but the dark spaces between the light stripes are always marked, interrupted or completely broken up by light spots or spaces, except in the young. The color variations are similar to those already mentioned under the head of the *C. tessellatus* but they are more numerous. Specimens from Western Texas come nearest in character to the *C. sexlineatus.* It takes the place of that species throughout Mexico, also replacing the *C. tessellatus* in the drier parts of that country. Besides the characters already cited, this species differs from the *C. tessellatus* in its finer scales. These measure from .25 to .33 mm. in diameter, while those of the *C. tessellatus* measure .5 mm.; but this character does not always hold good.

The subspecies of the *Cnemidophorus gularis* differ as follows:

Stripes persistent, narrow, defined; no black spots; femoral scales in 6–8 rows; hind legs yellow spotted, and with a stripe behind; smaller.............................. *C. g. gularis.*

Stripes persistent, wide, ragged; spots in interspaces irregular; parietal plate very narrow; muzzle elongate; legs neither spotted nor striped; large; 8 rows femoral scales; 6 infralabials, *C. g. angusticeps.*

Stripes vanishing, their interspaces with black crossbars ultimately joining crosswise; femoral scales 8–10; hind legs spotted; infralabials 5–6; large.................... *C. g. mariarum.*

Stripes broken up into rows of spots; interspaces with yellow spots; hind legs with or without yellow spots; no posterior femoral stripe; a frenoörbital; 5–6 infralabials; large, *C. g. communis.*

Light stripes traceable anteriorly only; black bands broken up into transverse spots by orange spots on body; hind limbs pale spotted; femoral scales 7–8 rows; infralabials generally 6; medium.............................................................. *C. g. scalaris.*

Anal plates 3–4; femorals in 8–9 rows; femoral pores 21; 6 infralabials; large scales of collar equal; stripes posteriorly obsolete; interspaces in front spotted; medium..... *C. g. sericeus.*

No light stripes; olivaceous with three rows of black spots on each side on anterior fourth of body; femorals 8; infralabials 6; muzzle elongate; limbs unspotted; medium, *C. g. semifasciatus.*

No light stripes ; olivaceous with black bars on sides which cross back on lumbar region ; rump and hind legs yellow spotted ; femoral scales 8 rowed ; infralabials 6 ; muzzle elongate ; medium.......................................................................... *C. g. costatus.*

The geographical distribution of the subspecies is as follows:

*C. g. gularis,* Sonoran region.
*C. g. angusticeps,* Yucatan.
*C. g. mariarum,* Tres Marias islands.
*C. g. communis,* S. W. Mexico.
*C. g. scalaris,* Chihuahua and southward.
*C. g. semifasciatus,* Coahuila, Mexico.
*C. g. costatus,* Mexico ; locality unknown.

These forms may be compared with those of the *C. tessellatus* in color characters as follows. I have already remarked* that this series of variations follows quite closely those pointed out by European authors to exist in the *Lacerta muralis.* These have been made the subjects of especial study by Prof. Eimer of Tübingen, from whose paper† I extract the following points of comparison (see Plate XII).

| | *Cnem. tessellatus.* | *Cnem. gularis.* | *Other Cnemidoph'i.* | *Lacerta muralis.* |
|---|---|---|---|---|
| 1. Longitudinally striped............ | *C. t. perplexus.* | | *C. octolineatus.*<br>*C. sexlineatus.* | *L. m. campestris.* |
| 2. Dark interspaces pale spotted...... | *C. t. tessellatus a.* | *C. g. gularis a.* | *C. labialis.* | |
| 3. Dark interspaces divided by light color.......................... | *C. t. tessellatus β.* | *C. g. scalaris a.* | *C. septemvittatus.*<br>*C. grahamii.* | *L. m. albiventris.* |
| 4. Dark spots confluent transversely, forming crossbars................ | *C. t. tessellatus γ.* | *C. g. scalaris β.* | | *L. m. striatomaculata.*<br>*L. m. reticulata.* |
| 5. Light spots not confluent; light stripes broken up ; pattern reticulated.......................... | *C. t. melanostethus.* | *C. g. costatus.* | *C. variolosus.* | *L. m. tigris.*<br>*L. m. punctulatofasciata.* |
| 6. Dark spots separate and on a brown ground......................... | *C. t. rubidus.* | *C. g. semifasciatus* | | |

There are some color forms in the *Lacerta muralis* which are not repeated in the North American Cnemidophori, particularly those which result in a strong contrast between the dorsal colors as a whole and the darker lateral colors, as a band. The color variety, No. 6, of the Cnemidophori is not reported by Eimer as occurring in the *Lacerta muralis.*

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* American Naturalist, Dec., 1891.

† Archiv. f. Naturgeschichte, 1881, 239.

## *Cnemidophorus gularis gularis* B. & G.

*Cnemidophorus gularis* Bd. Gird., Proceeds. Acad. Phila., 1852, p. 128.
Baird, U. S. Mex. Bound. Surv. Rept., Pl. XXXIV, Figs. 1–6.
*Cnemidophorus guttatus* Hallowell, Proceeds. Acad. Phila., 1854, p. 192.

This form resembles the Sexlineatus more than any other, but always possesses the postantebrachial plates, and more numerous femoral pores, which range from eighteen to twenty-two. Occasional specimens are, however, intermediate between the two. Its range is the Sonoran region.

Under this subspecies must be placed four of the series of forms which I described in my paper on the Reptilia of Chihuahua as subspecies of the *C. sexlineatus*,* in the following language; two of the forms (Nos. 5, 6) being the *C. g. scalaris* M.:

"1. Six longitudinal narrow stripes with unspotted interspaces................*C. g. gularis* (young).
2. Six stripes as above, the dark interspaces with small white spots..........*C. g. gularis verus.*
3. Six stripes as above, wider and very obscure; small obscure spots .....*C. g. gularis obsoletus.*
4. Six stripes as above, but wider, and the spots enlarged so as to be confluent occasionally with the light stripes.....................................................

"Of the above forms all are numerously represented in the collection. The modification of the color pattern described, is not entirely due to age, as some of the largest specimens belong to Nos. 2 and 3. Nevertheless small specimens predominate in the No. 1, and No. 4 presents a good many small specimens." The specimens enumerated are as follows: †

Subspecies No. 1; Nos. 14,236–41–49–69; 14, 305.
Subspecies No. 2; 14,231–41,305–308.
Subspecies No. 3; 14,231–50–308.
Subspecies No. 4; 14,241–50–302–5.

These forms are not sexual, as several of them include both sexes.

Not having been fully persuaded of the distinction between the *C. tessellatus* and *C. sexlineatus* series, I used the name *C. s. tigris* for a "sixth subspecies" of the above table. The name was however misapplied, although the color pattern is identical with that of the *C. tessellatus tigris* B. & G., with the exception that there are traces of six stripes instead of only four. The smaller specimens referred to the *C. s. sexlineatus* differ from that subspecies in having well-developed postantebrachial scales.

The gradation in the color characters given is complete, so that no subdivision into subspecies can be made. The case is exactly parallel with that of *C. tessellatus*

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* Proceeds. Amer. Philos. Soc., (1885) 1886, p. 283.

† The numbers are attached to lots, by the recorder, and not to individuals, and are hence sometimes duplicated.

*tessellatus*, except that there are here no individuals with the stripes entirely obliterated, and complete transverse stripes posteriorly. (Such specimens are the *C. g. scalaris;* see below.) The femoral pores are generally eighteen, but some have sixteen, seventeen and twenty. In eleven of the specimens now before me, seven have five infralabials, and four have six. These numbers do not coincide with the color types.

### *Cnemidophorus gularis angusticeps* Cope.

Boulenger, Catal. Liz. Brit. Mus., II, 1885, p. 366.
*Cnemidophorus angusticeps* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 95.

This large form is easily recognizable by its peculiar coloration, and by the very narrow parietal plate, which is about three times as long as wide. Four specimens are in the U. S. National Museum from Yucatan.

### *Cnemidophorus gularis mariarum* Gthr.

*Cnemidophorus mariarum* Günth., Biologia Centr. Amer. Rept., p. 28, Pl. XX.

This also large form is distinguished from the other subspecies by the larger number of rows of its femoral plates, and by the coloration. In the young the dark spaces between the light stripes are crossbarred with black instead of a light color as in the other forms, and the result is crossbars on the sides in the adults, on the disappearance of the stripes. The hind legs are covered with large round yellow spots. The color pattern of this form corresponds with the *Lacerta muralis maculostriata* of Eimer.

Two specimens are in the U. S. National Museum, one from the Tres Marias islands, the typical locality, and the other of uncertain origin.

### *Cnemidophorus gularis communis* Cope.

*Cnemidophorus communis* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 95.

This subspecies reaches a larger size than any of the others of the *C. gularis*, and its peculiar coloration of small (or sometimes large) yellow spots on a dark olive ground, gives it a very distinct appearance. This form is identified with doubt with the *Cnemidophorus mexicanus* of Peters by Bocourt. What Peters' species is I have been unable to ascertain.

About forty specimens were sent to the National Museum from Colima, Western Mexico, by J. Xantus.

## *Cnemidophorus gularis scalaris* Cope.

American Naturalist, 1891, p. 1135; (published March 1, 1892).
*Cnemidophorus sexlineatus tigris* "B. & G." Cope, Proceeds. Amer. Philos. Soc., 1886, p. 283; not *C. tigris* B. & G.

Muzzle moderately acuminate in adults; frenal plate about as high as long; frenoöcular plate generally wanting. Brachial scales small, in eight rows; antebrachials in three; postantebrachials in two or three rows. Femorals in eight rows. The three large anal plates are bounded by several small plates laterally and in front. Femoral pores nineteen; in one eighteen, and in one seventeen. Longest toe of extended posterior leg reaching to front of auricular meatus. First and fifth toes measuring opposite to each other.

Ground color pale, on the sides posteriorly light rosy orange. The dark color only remains as narrow transverse black stripes which do not cross the middle line, which is occupied by a longitudinal series of spots. This is due to the fact that in the adults the black ground is completely broken up by the transverse extensions of the light stripes, which are quite traceable in the young. In some specimens the black spots do not fuse on the sides into transverse stripes (No. 14,302). All the dark markings fade out on the limbs and sacral region, leaving a gray ground (in alcohol) which is marked with rosy orange spots. The lateral ventral plates and all those of the thorax with the posterior or concealed face of the anterior leg, are black or blackish in the adult.

Measurements of adult (tail injured): Length to vent 93 mm.; do. to angle of mandible 25 mm.; do. to collar 29 mm.; do. to axilla 26 mm. Length of anterior limb 30 mm.; do. of fore foot 14 mm. Length of hind limb 67 mm.; do. of hind foot 37 mm.

Several specimens of this form are contained in the collection, and they agree closely in all respects. In coloration it is perhaps the most ornamental of the genus. It is well distinguished from the *C. grahamii* in color characters, as well as in the presence of the well-developed postantebrachial scales. In the *C. gularis* it corresponds exactly in color characters with the *tigris* form of the *C. tessellatus tessellatus*, designated in the plate of colors (XII) as D and E.

*Cnemidophorus gularis scalaris* Cope.

| *Catalogue Number.* | *Number of Specimens.* | *Locality.* | *From whom obtained.* | *Nature of Specimen.* |
|---|---|---|---|---|
| 8,319 | 5 | Mexican Plateau S. of Chihuahua. | J. Potts. | Alcoholic. |
| 14,302 | 2 | City of Chihuahua. | Edw. Wilkinson. | Alcoholic. |

### *Cnemidophorus gularis sericeus* Cope.

Scales of the collar moderate, subequal, in four or five rows, marginal scales equal to the others. Mesoptychial scales considerably smaller than the gular scales, which are large, and extend from one ramus to the other. Scales of the back rounded, not prominent, small, measuring .033 mm. Supraorbital plates wider than long except the anterior, and not separated from the frontoparietals by scales. Interparietal large, not twice as long as wide; parietals subtriangular, as wide as the interparietal, but much shorter. Frontoparietals remarkable for their small size, and from their terminating each in an angle anteriorly, which receive between them the posterior apex of the unusually narrowed frontal. They are smaller than the parietals, which are smaller than in other species. If these characters prove constant, I shall regard this form as a true species. Infralabial plates six on each side, the last one small; the first pair separated at the posterior angle. Brachial scales in six rows; antebrachials in four. Femorals in eight, tibials in three rows. Femoral pores twenty-one. The hind limb extended reaches the posterior border of the orbit.

Size medium. Length of head and body (tail injured) 81 mm.; length to angle of mandible 22 mm.; to edge of collar 26 mm.; to axilla 31 mm.; to fore limb 26 mm.; of fore foot 14 mm.; of hind leg 60 mm.; of hind foot 32 mm.

Ground color above anteriorly black, posteriorly olive. This is marked by six narrow lines of a paler olive, which represent the lines of the *C. sexlineatus*, with an additional median dorsal one. These fade out or become very indistinct on the lumbar and sacral regions. The interspaces black anteriorly, are marked at first by small olive spots, but these enlarging, break up the black ground into spots, but these fade out on the middle of the length. The superior surfaces of the limbs and tail are olive, the latter unspotted; the hind limbs faintly spotted with paler above and posteriorly, and the forearm reticulated with black posteriorly. The dorsal stripes, except the three median, extend as far as the orbit. Rest of head olivaceous. Lower surface of head, limbs and tail, yellow, the first named with a bluish transverse patch across the gular region.

This species has various peculiarities. It differs from the other members of the *C. gularis* series in the larger number and more equal size of the scales of the gular fold, approaching in this way the *C. tessellatus*, but not agreeing with it, since the marginal scales are not smaller. It differs from all the species in the small size of the interparietal and parietal plates. Its posterior legs are longer than in any species except the *C. variolosus*. No species has four rows (or three at the narrowest part) of antebrachial scales; the usual number being 3–2; and the femorals are more numerous than in the *C. g. gularis*. The coloration is also quite distinctive. But one specimen is known, and that is from Southwestern Texas. The discovery of other specimens will determine whether this is or is not a true species. In the obsolescence of the color pattern posteriorly it resembles the *C. g. semifasciatus*, following.

*Cnemidophorus gularis sericeus* Cope.

| *Catalogue Number.* | *Number of Specimens.* | *Locality.* | *Whence obtained.* | *Character of Specimen.* |
|---|---|---|---|---|
| 15,650 | 1 | San Diego, Tex. | Wm. Taylor. | Alcoholic. |

## *Cnemidophorus gularis semifasciatus* Cope.

Muzzle compressed, rather elongate; frenal with frenoöcular, longer than high. Large scales of the collar confined to the middle portion, smaller scales appearing on each side, and granules on the edge of the collar laterally. Posterior supraorbital small and divided on both sides, perhaps abnormally. Interparietals as wide as parietals, and extending farther posteriorly. Larger scales behind parietals few in number. Brachial scales in six, femorals in six rows. Postantebrachials in three or four rows. Femoral pores twenty. Dorsal scales minute. Anal plates three large ones with eight to ten smaller ones on the sides and in front. The hind leg a little short, the longest toe, when extended, not reaching the *meatus auditorius* by the diameter of the latter.

Total length 300 mm.; do. to angle of mandible 25 mm.; do. to collar 32 mm.; do. to axilla 42 mm.; do. to vent 100 mm. Length of fore limb 30 mm.; do. of fore foot 13 mm.; do. of hind leg 64 mm.; of hind foot 36 mm.

The color is uniform olivaceous above and below, with the following black marks: There are three rows of black spots on each side of the middle line above; the superior small, subquadrate, the second larger and transverse, the inferior forming short crossbars. The superior row extends from the interscapular region to the middle of the length of the back; the second row extends farther and the inferior row extends nearly to the groin. Limbs, head, belly and tail unspotted.

This form has various peculiarities which entitle it to be regarded as a subspecies, and possibly as a species. But two specimens are known to me. In No. 3033 the black spots are smaller, and are restricted to the anterior fourth of the length of the body, being most distinct in front of the scapular region. Here traces of the original six stripes are visible between the spots.

It is possible that it may be demonstrated that the *C. sericeus* is established on a female of this species with abnormally reduced frontoparietal plates. The coloration is much like that of specimen No. 3033.

*Cnemidophorus gularis semifasciatus* Cope.

| *Catalogue Number.* | *Number of Specimens.* | *Locality.* | *Whence derived.* | *Nature of Specimen.* |
|---|---|---|---|---|
| 9248 | 1 | Coahuila, Mex. | Lieut. Couch. | Alcoholic. |
| 3033 | 1 | Patos Coahuila. | Lieut. Couch. | Alcoholic. |

## *Cnemidophorus gularis costatus* Cope.

*Cnemidophorus sexlineatus costatus* Boulenger, Catal. Liz. Brit. Mus., II, 1885, p. 366.
*Cnemidophorus costatus* Cope, Proceeds. Amer. Philos. Soc., 1877, p. 95.

This form is totally distinct from all others in coloration. There are six infralabials and eighteen femoral pores in the only known specimen. This is about the size of a large *C. s. gularis*, or less than the *C. s. angusticeps* and *communis*. Exact habitat unknown, but it is Mexican.

## CNEMIDOPHORUS OCELLIFER Spix.

Peters, Monatsber. Akad. Wiss. Berlin, 1877, pp. 412–14.
Boulenger, Catal. Liz. Brit. Mus., II Ed., 1885, p. 372.
*Tejus ocellifer* Spix, Spec. Nov. Lacert. Braz., p. 23, Pl. XXV.
*Cnemidophorus hygomii* Rhdt. et Lütk., Vidensk. Meddel., 1861, p. 231.
Bocourt, Miss. Sci. Mex. Rept., Pl. XX$^c$, Fig. 12.
Brazil.

## CNEMIDOPHORUS MULTILINEATUS Philippi.

Archiv f. Naturgesch., 1869, p. 41.
Boulenger, Catal. Liz. Brit. Mus., 2d Ed., II, 1885, p. 373.
From Mendoza, Argentina.
Unknown to me by autopsy.

### CNEMIDOPHORUS LABIALIS Stejneger.

Proceeds. U. S. Nat. Museum, XII, p. 643.

This is the smallest species of the genus, and is well characterized by its scutal peculiarities.

Cerros Id., coast of Lower California.

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## EXPLANATION OF PLATES.

Each plate includes the following figures: Superior, inferior and lateral aspects of head; superior view of arm and inferior view of forearm; inferior view of hind leg, with anal region; scales from side of body, with borders of ventral plates. The figures are natural size except

NOTE.—For the greater part of the material on which this paper is based, I am indebted to the U. S. National Museum, and its distinguished directors, Profs. S. P. Langley and G. Brown Goode.

### *Plate VI.*

Fig. 1. *Cnemidophorus tessellatus perplexus* B. & G.; Specimen No. 3060 U. S. Nat. Museum.

Fig. 2. *Cnemidophorus tessellatus tessellatus* Say, *α;* Spec. No. 3041 U. S. Nat. Museum.

### *Plate VII.*

Fig. 3. *Cnemidophorus tessellatus tessellatus* Say, *β*; No. 4113 U. S. Nat. Museum.

Fig. 4. *Cnemidophorus tessellatus tessellatus* Say, *γ*; No. 3048 U. S. Nat. Museum.

### *Plate VIII.*

Fig. 5. *Cnemidophorus tessellatus melanostethus* Cope; No. 3067 U. S. Nat. Museum.

Fig. 6. *Cnemidophorus variolosus* Cope; No. 3060 U. S. Nat. Museum.

### *Plate IX.*

Fig. 7. *Cnemidophorus sexlineatus* Linn.; No. 4878 U. S. Nat. Museum.

Fig. 8. *Cnemidophorus septemvittatus* Cope; No. 2872 U. S. Nat. Museum.

### *Plate X.*

Fig. 9. *Cnemidophorus gularis gularis* B. & G.; No. 3039 U. Nat. Museum.

Fig. 10. *Cnemidophorus gularis scalaris* Cope; No. 8319 U. S. Nat. Museum.

## *Plate XI.*

Fig. 11. *Cnemidophorus scalaris sericeus* Cope ; No. 3066 U. S. Nat. Museum.
Fig. 12. *Cnemidophorus gularis semifasciatus* Cope ; No. 9248 U. S. Nat. Museum.

## *Plate XII.*

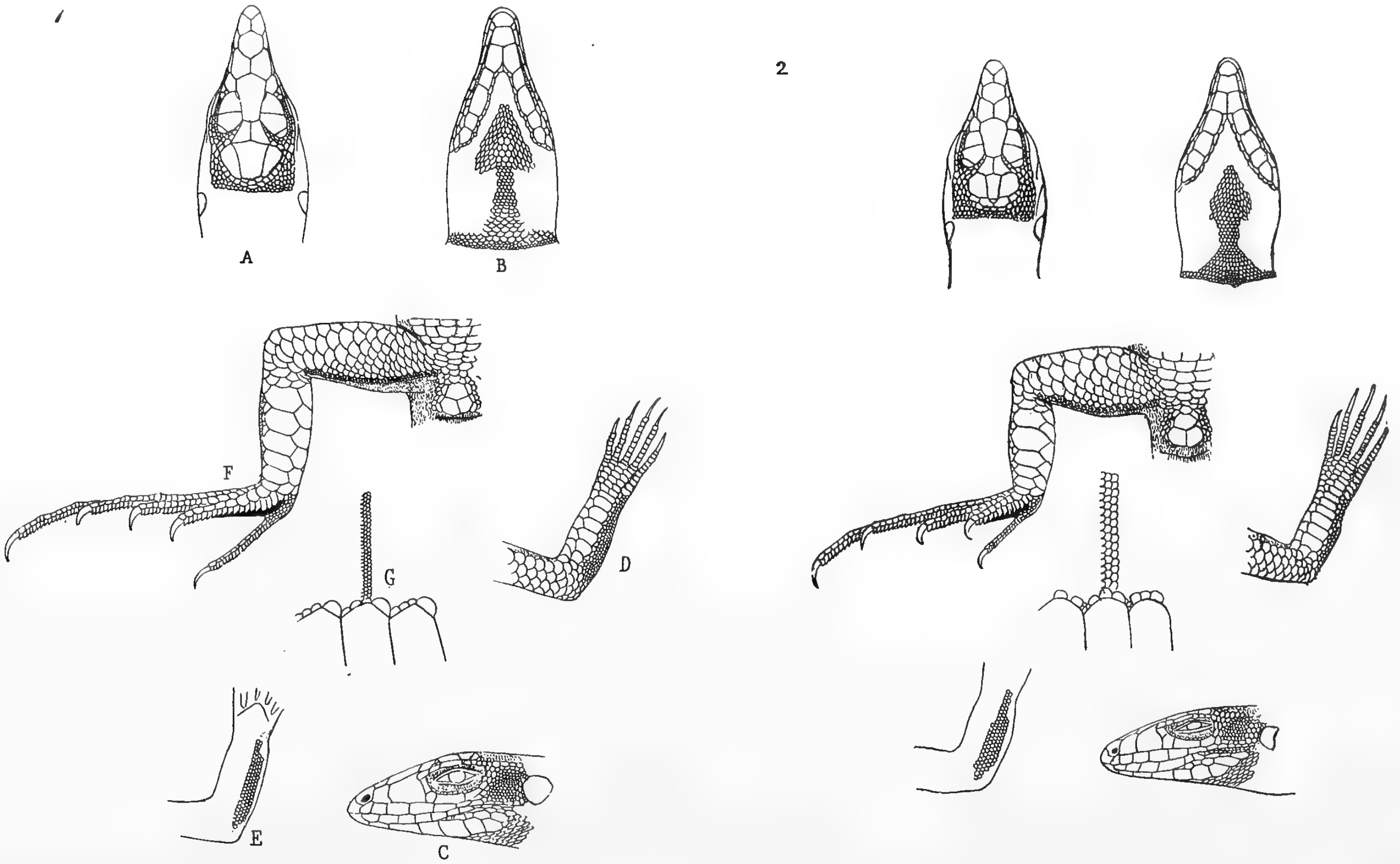
Color variations of *Cnemidophorus tessellatus* and of *Cnemidophorus gularis.*

*A.* Young of *C. tessellatus* (*C. gracilis* B. & G.); No. 9270.
*B.* *C. tessellatus perplexus* B. & G.; No. 3060.
*C.* *C. tessellatus tessellatus* Say, *β*; No. 3048.
*D.* *C. tessellatus tessellatus*, *γ*; No. 4113.
*E.* *C. tessellatus tessellatus*, *δ*; No. 3048.
*F.* *C. tessellatus rubidus* Cope; No. 15,149.
*G.* *C. gularis gularis;* young; No. 14,249; and adolescent (sp. from Rio Grande, Capt. Livermore).
*H.* *C. gularis gularis* B. & G.; adult; No. 3039.
*I.* *C. gularis scalaris* Cope, *α*; No. 14,302.
*K.* *C. gularis scalaris* Cope, *β*; No. 8319.
*L.* *C. gularis semifasciatus* Cope ; No. 9248.

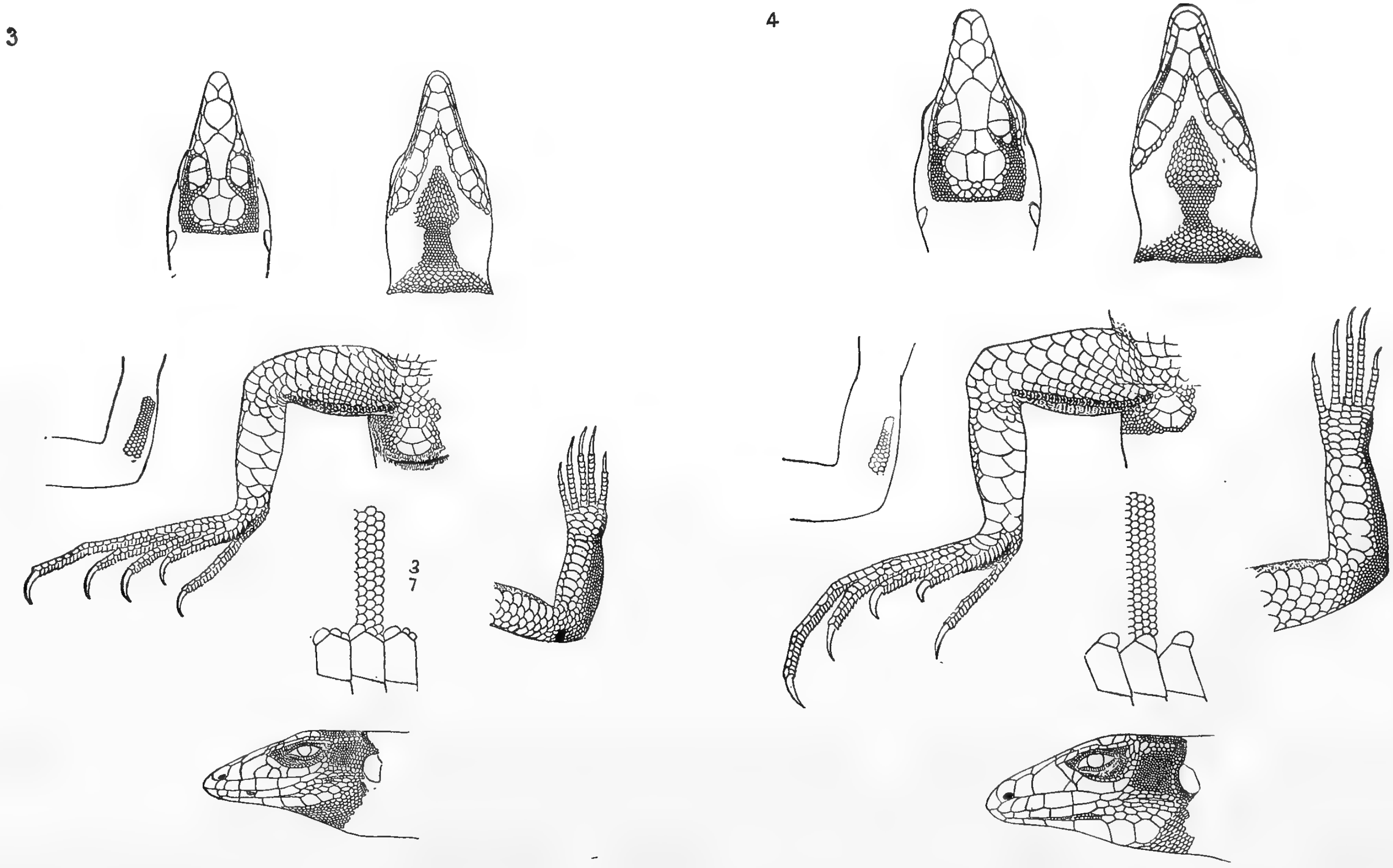
## *Plate XIII.*

Color variations of *Lacerta muralis* copied from Eimer.

*A.* *Lacerta muralis ;* young; from Karst.
*B.* *L. m. campestris* De Betta.
*C.* *L. m. albiventris* Bonap.
*D.* *L. m. maculata* Eimer.
*E.* *L. m. tigris* (*reticulata*) Eimer.

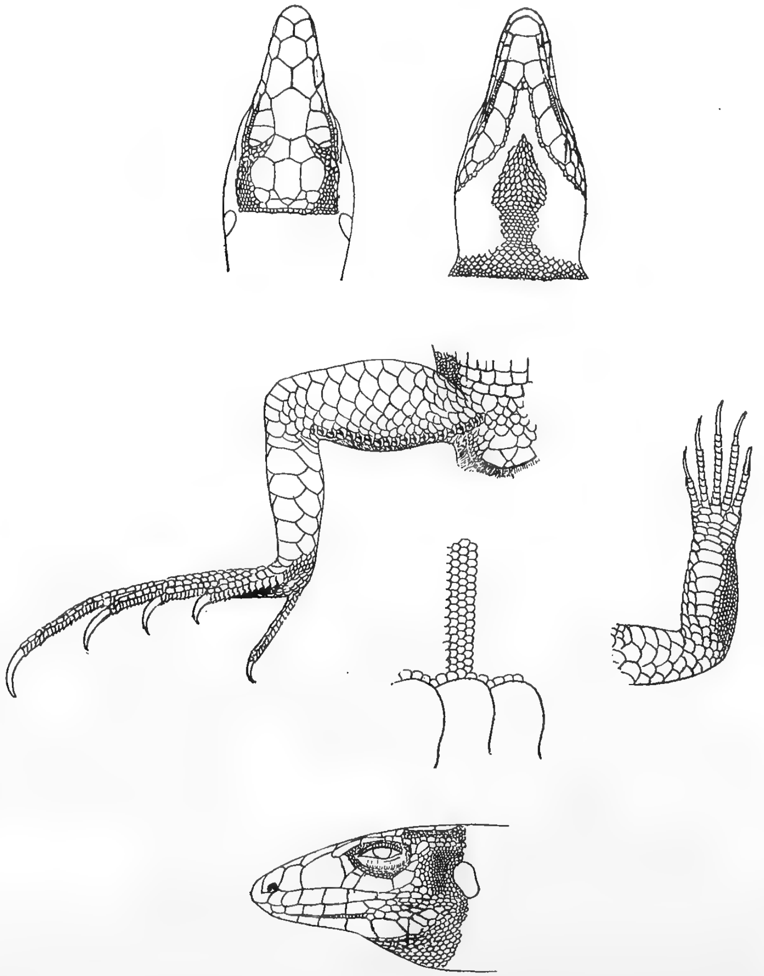


1, Cnemidophorus tessellatus perplexus. 2, C. t. tessellatus *a*.

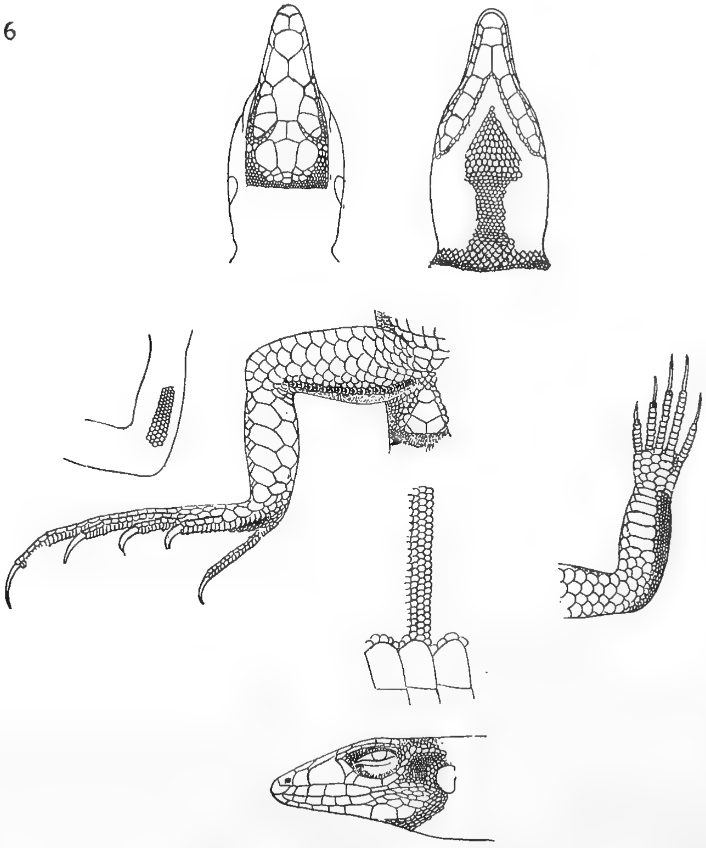


3, Cnemidophorus tessellatus tessellatus β. 4, C. t. tessellatus γ.

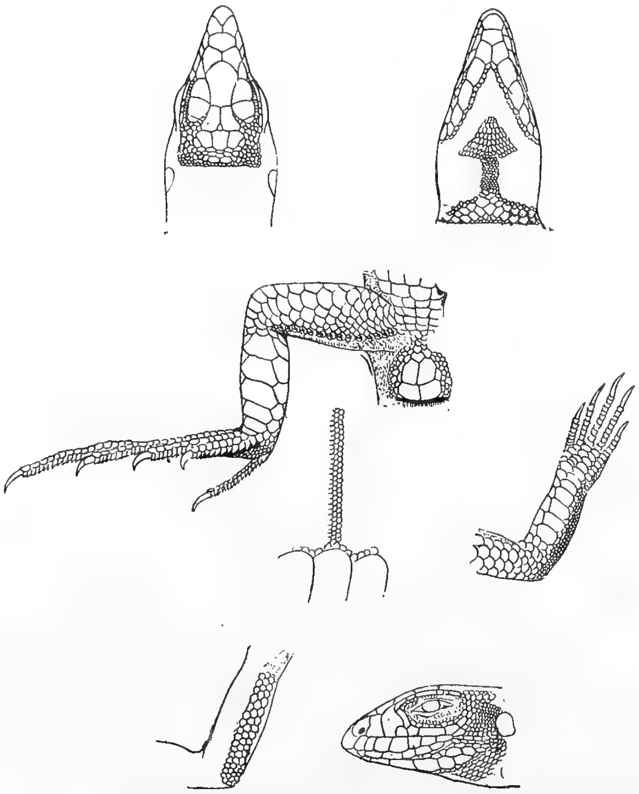
5



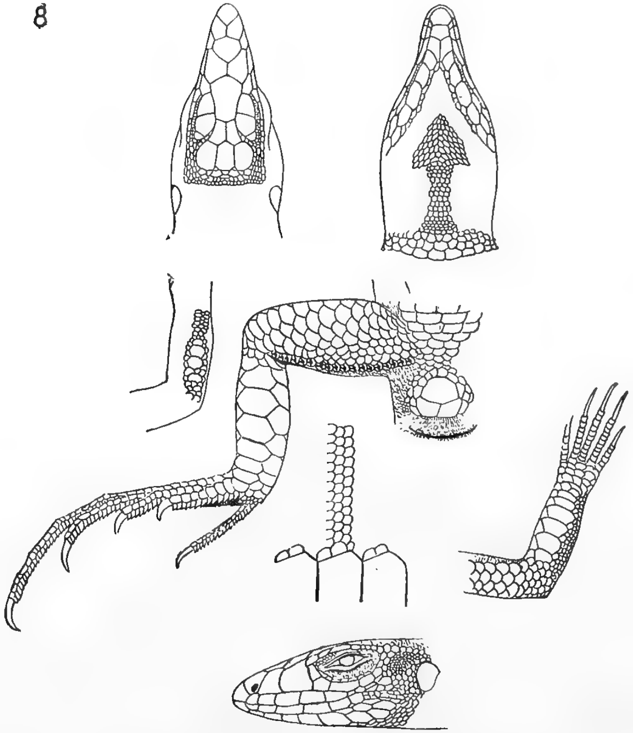
6



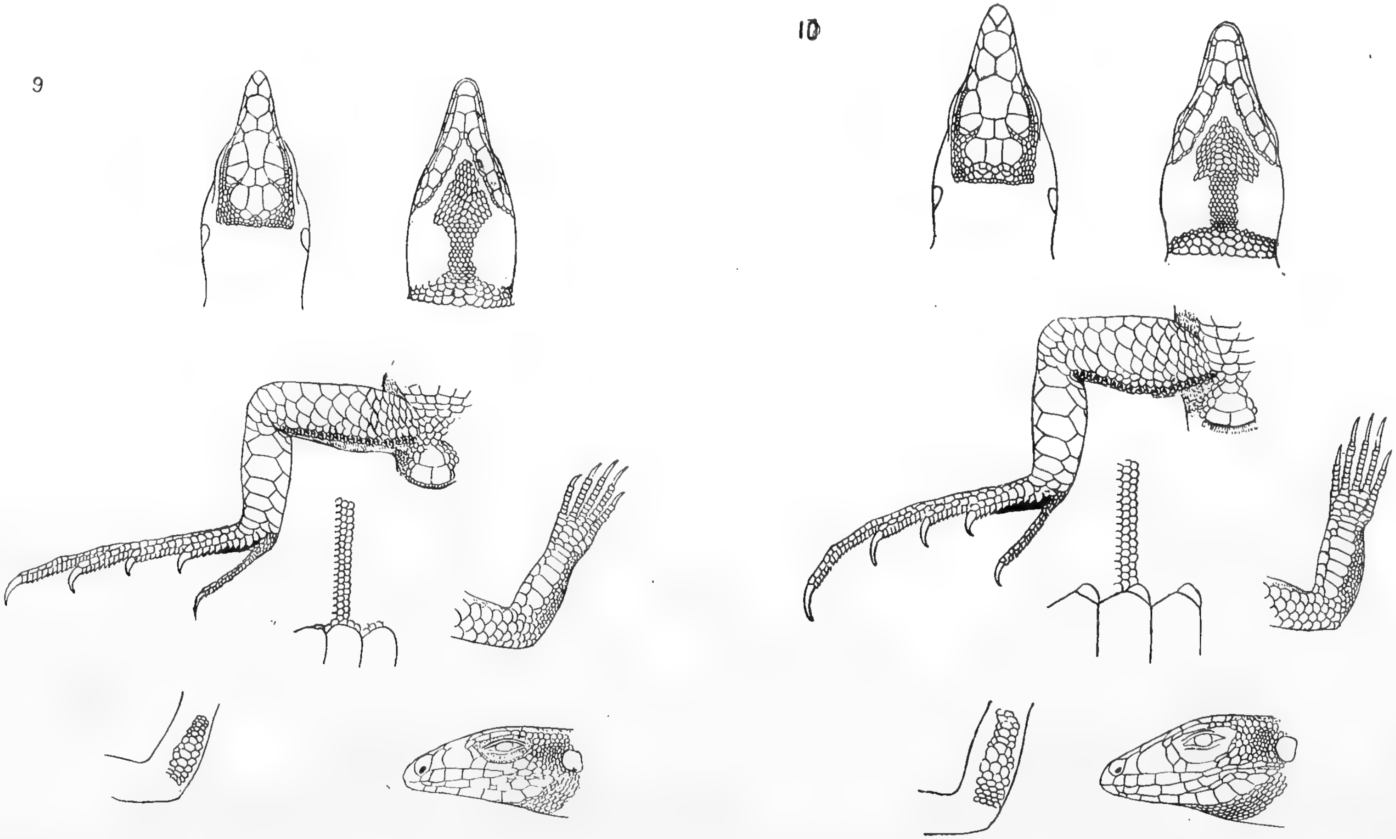
5, Cnemidophorus tessellatus melanostethus. 6, C. variolosus.



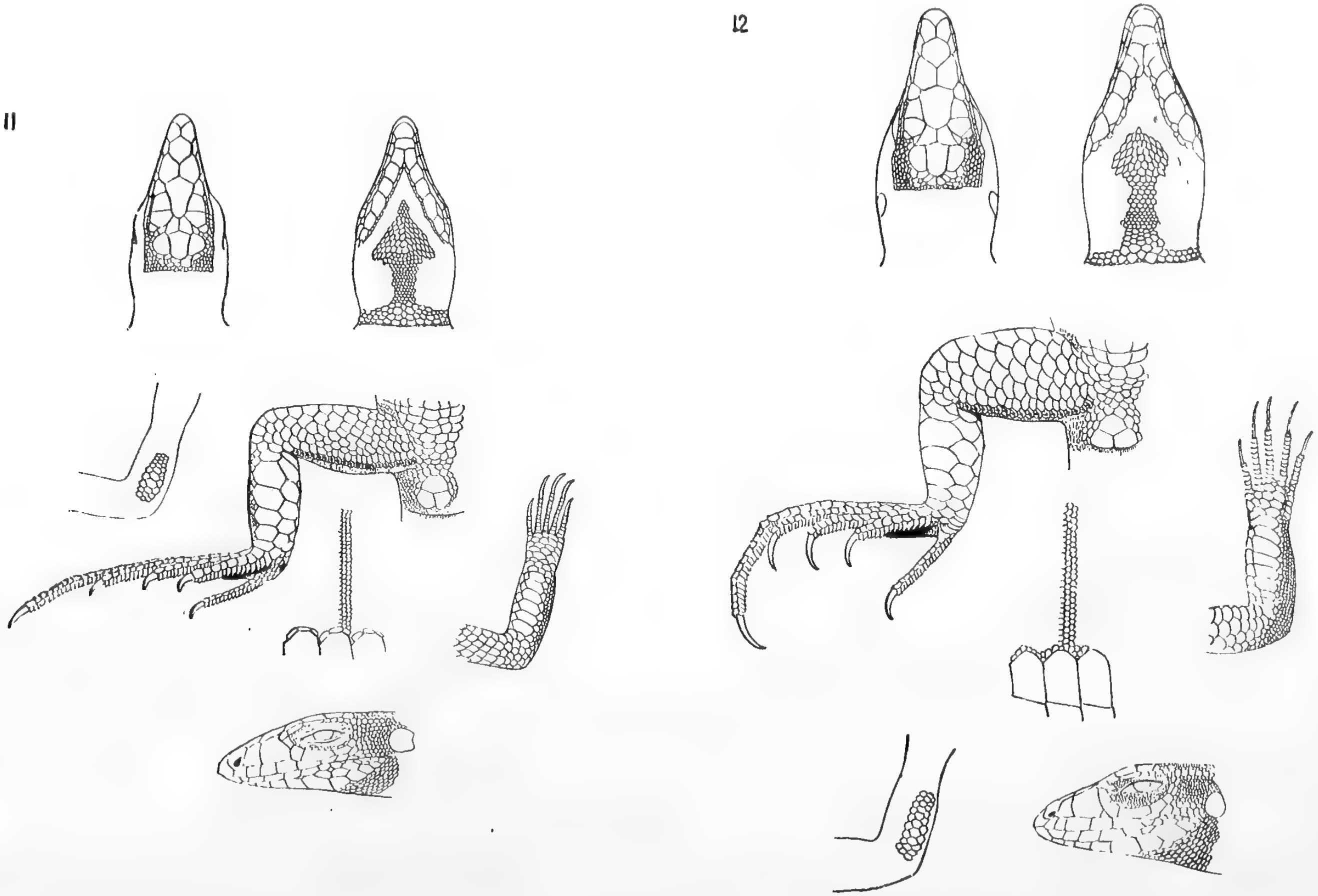
8



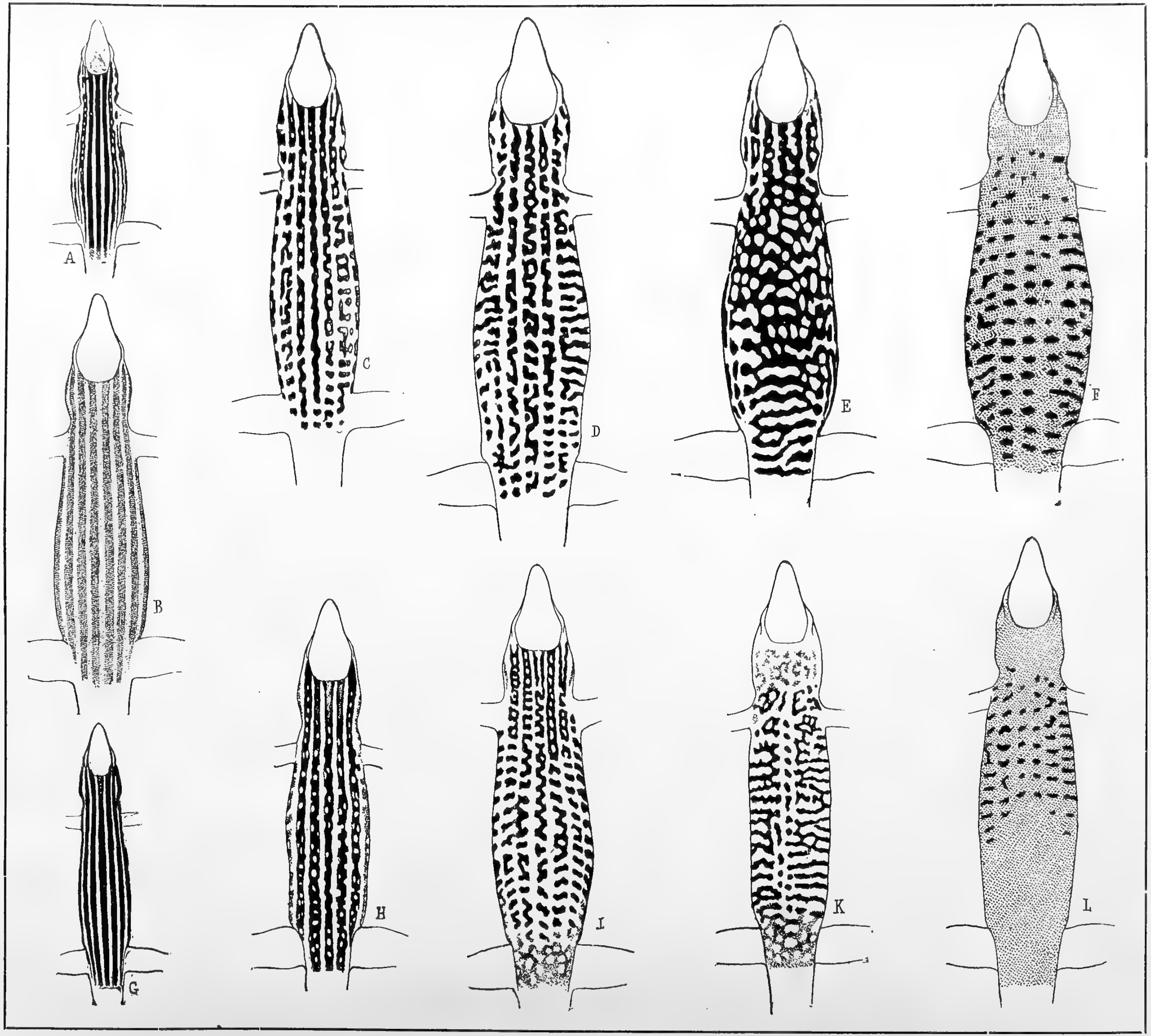
7, Cnemidophorus sexlineatus. 8, C. septemvittatus.



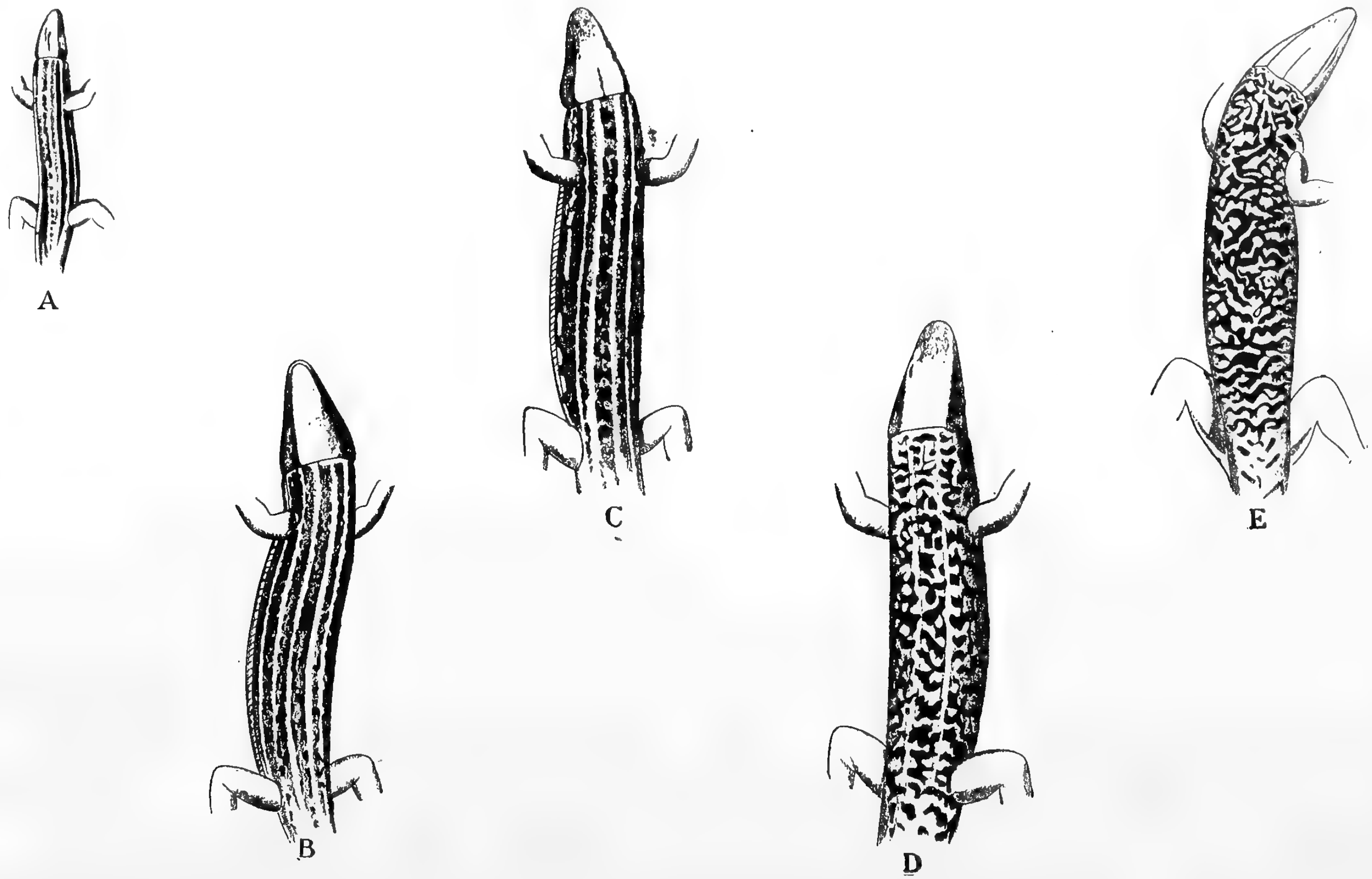
9, Cnemidophorus gularis gularis. 10, C. g. scalaris.



11, Cnemidophorus gularis sericeus. 12, C. g. semifasciatus.



*A–F*, Cnemidophorus tessellatus. *G–L*, C. gularis.



*A–E*, Lacerta muralis.

# ERRATUM.

Page 59, line 12 from bottom, *for* "Tepetlaplalco" *read* "Tepetlatlalco."

Page 60, line 10 from top, *for* "No. 2" *read* "No. 1."

# ARTICLE IV.

## THE TRIBUTE ROLL OF MONTEZUMA.

EDITED BY
Dr. DANIEL G. BRINTON, Chairman,
HENRY PHILLIPS, Jr., and
Dr. J. CHESTON MORRIS,
A Committee appointed by the American Philosophical Society, November 16, 1888.

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## Part I.

### THE WRITTEN LANGUAGE OF THE ANCIENT MEXICANS.

BY DANIEL G. BRINTON, M.D., LL.D.

There are scarcely any tribes, however rude, who do not aid their memory by some objective device. The savage Australians have tally sticks, and in some localities depict figures on the walls of caves in honor of some important event. A handful of sticks of different lengths was the simple mnemonic device of the Iroquois; while knots tied in strings led in Siberia and Peru to a complicated system of thought recording.

The arts of drawing and coloring lent themselves with peculiar facility to this purpose. They were by no means late or limited acquisitions of the human intellect. Far back in Palæolithic times we find evident traces of them, as we also do amongst savage peoples in every continent. The man of the mammoth and the reindeer epoch depicted these animals with singular fidelity by scratching their outlines on bones; and the paint pots and masses of ochreous earth found on the sites of his dwellings prove that he was also a colorist, though his canvas may have extended little beyond his own skin. On this he probably drew and painted, as does the savage to-day, some signs or marks which designated to what clan he belonged, or of what deeds he was proud. If his family was that of the bear, he would draw the outline of a bear; if he boasted of his hunting exploits, he would depict the outlines of a man spearing an animal.

Just such devices do we find on fragments of bone and stone dating from the Magdalenian epoch in France. They are the beginnings of recorded language, the primitive examples of writing. In such instances of picture writing, the outline of the bear recalled the concept, bear, and this is the utmost that any form of writing can do.

Picture writing was familiar to almost all American tribes. It is the simplest and first step to all stages of recorded thought; but it is cumbrous, and inapplicable to many ideas. We cannot directly depict what is abstract, or a general term, or a complex conception. This deficiency led to the employment of *symbolic* characters. In these, a part is taken for the whole of a picture, as a foot of a rabbit for the rabbit itself; or the figure of the sun, the life-giver, for the abstract idea of life—both which symbols occur in the native Algonkin writing. In time, the symbol became conventionalized in form, so that the connection which originally existed between it and a concrete conception was lost from sight and memory. The figure of forgotten origin represented an idea, and this was all that was known about it. Thus arose ideographic writing, such as we find in singular development among the Chinese.

Still, it will be observed, there is no relation of any of these signs to the sound of the language. All of them—pictorial, symbolic and ideographic—bear no more relation to the spoken word than do the Arabic numerals to us. An ideographic text, like an algebraic formula, can be read by all who have once been taught the meaning of its elements. It is a universal language. This immense advantage is more than counterbalanced by the enormity of the task of committing to memory the necessary number of ideograms requisite for the purposes of life. It is said that in China at least five thousand characters are needed to conduct a business of ordinary extent; and that a man of learning should be able to recognize twenty to thirty thousand. Few men in life require a knowledge of more than three languages; while the great majority have no use for more than one. Hence a method which represents all the concepts in a language by the combination of thirty or forty characters is incalculably more time-saving, and therefore better for the vastly greater number, than one which demands thousands of characters.

This obvious advantage made itself felt early in the history of writing. The most ancient Pyramid texts of Egypt, the oldest Cuneiform of Syria, indicate the effort of the human mind to seek a way out of the cumbrous fetters of thought-writing into a freer air, by having the sign no longer refer to the thing or the thought but to the *sound*, the spoken word.

These general remarks are not out of place in this connection; they are in fact necessary, for the method of writing developed by the ancient Mexicans, in the stage in which it existed at the time of their subjection by the Europeans, embodied, curiously enough, every one of these elements, pictures, symbols, ideograms and phonetic signs; and it is only by keeping this fact constantly in mind, and by seeking to render each according to the special system which it represents, can we hope ever to untangle the labyrinth of the Aztec codices.

It is because this essential fact has been overlooked that the syllabaries and lists of Mexican hieroglyphs hitherto published have proved almost worthless for the decipherment of the manuscripts which have been preserved. It must also be observed that the same sign may have a phonetic value in one place, and a purely ideographic in another; and it would be obviously absurd for any scholar to attempt the construction of such a syllabary unless he is familiar with the sounds of the Nahuatl as a spoken tongue. Otherwise the phonetic elements would escape him.

The presence of all these various methods of writing in the same document can readily be demonstrated. No one will question that in the tribute rolls, such as the Codex Mendoza, published in Lord Kingborough's collection, the picture of a feathered coat, or some such definite object, followed by the well-known signs of the numerals, means that a certain number of such articles were due from a certain district. Here the coat is in picture writing, while the numerals are ideograms. Again, where in the year signs, the rabbit, *tochtli*, is represented by his head only, we have a symbol.

There has been no dispute among students of Mexican hieroglyphs that signs of these several characters occur; but when it comes to the alleged presence of purely phonetic elements, the divergence of opinion has been considerable. Some writers have claimed that a large proportion of the figures refer to sounds rather than thoughts, while others have gone so far as to deny all evidence of phoneticism in the codices.

Much of this discrepancy has arisen from the tendency of students of the latter class to look in the Mexican writing for an alphabet, like that to which we are accustomed. Nothing of this kind existed, or could exist in the stage to which the Aztecs had developed their plan of recording thought. The material out of which an alphabet might have evolved was indeed present, but it was submerged in much extraneous and traditional rubbish.

The line of research which I believe will give us the clue to a correct interpretation of the phonetic elements in the Mexican codices I have set forth and exemplified with a number of illustrations in some articles published several years ago and collectively republished in my "Essays of an Americanist" (Philadelphia, 1890). A brief statement of the method there advanced may appropriately be introduced here.

It is agreed among those who have most carefully studied the subject that there is but one path by which the human mind could have originally proceeded from ideographic or thought writing to phonetic or sound writing. This was through the existence of homophones and homoiophones, that is, of words with different meanings but the same or nearly the same sound. The same sign would come to represent two different ideas, not that it represented them both pictorially, but because both were expressed in the language by the same sound. This is the secret of the first introduction of the element of sound into writing.

An illustration of this may be offered from the Egyptian writing in its early stage. The word *nefer* meant a lute, and in the early texts when the writer wished to convey the idea of a lute he simply drew the picture of one, and all understood it and read it *nefer*. But this sound *nefer* had in Egyptian another meaning, which was "door;" just as in English the sound *lute* has also the meaning booty or plunder (loot). It was discovered therefore that by reference to sound the picture of a lute could also stand for "door" and thus save the trouble of having a separate sign for that concept. Proceeding on this line the same figure would come to be employed for a number of ideas expressed in the spoken tongue by the same or closely similar sounds; as in fact the sign of the lute in Egypt came to signify not only a lute or a door, but a soldier, a colt and the adjective "good."

When the word thus represented was a monosyllable, the sign for its sound would apply not only to it but also to all words in the language where this syllable occurred; and thus a syllabic alphabet began to be developed. Again, when this monosyllable coincided with one of the phonetic radicals of the language, that is, with one of the letters of its natural alphabet, we perceive the beginning of the true alphabetic writing. A simple example of this would be in English the picture of a bee, which in sound represents the second letter of the English alphabet.

The discussion of these distinctions is not irrelevant to the present theme. On the contrary, the student must have them constantly in mind, for as he investigates the phonetic elements of the Mexican codices, he will find that sometimes they represent the whole of a polysyllabic word, at other times a syllable only, and more rarely, that a true phonetic radical had been evolved and was employed just as we employ a letter of our alphabet in writing a word. I believe it may be averred with safety that of the five vowels and fourteen consonants which make up the Nahuatl alphabet, three vowels and three consonants had reached the stage where they were treated as true letters. The vowels were *a* for which the sign was borrowed from the term *atl*, water in composition *a;* *e* was represented by a bean, *etl*, in composition *e;* and *o* by a footprint or path, *otli*. The consonants were *p*, represented by a flag, *pan*, or a mat, *petl;* *t* by a stone, *tetl*, or the lips, *tentli;* and *z* by a lancet, *zo*. As in the case of *p* and *t*, several signs were employed for the same sound, no uniformity having been established in this respect. This is especially true for the syllabic characters, where there was a still wider range of variation, much depending on the caprice or the habit of the scribe.

These variants offer difficulties enough to the student; but they are light compared to what is further in store for him.

When the whole name of an object or most of it was used as a phonetic value, and several such pictures representing sounds are brought together to form a sentence or compound word, the script remains truly phonetic, but becomes a regular puzzle, in all respects of the character of that which we call a Rebus.

This principle is also that which is seen in the "canting arms" of mediæval heraldry, and is at the basis of most of that play upon words which we call "punning." So far as I am aware, there is no term in science which serves to express it, and for this reason in the articles above referred to I gave it the name *ikonomatic* writing, that is, a method of writing by means of the names of the figures or objects represented. It resembles in appearance, but differs radically in principle, from picture writing, for although it is composed of pictures, these in ikonomatic writing are used solely with reference to the sound of their names, and not with any relation to the objects which they portray.

Since my publications on this subject, Dr. Morris Jastrow, Jr., has called attention to a number of examples probably of the same character, in Assyrian inscriptions; and it would appear to have been one of the stadia through which human art passed in its efforts to develop a true alphabet. Its undoubted presence and extensive employment in the Mexican system of writing I have abundantly shown in the articles to which I would refer the reader who would desire further evidence.

While it is my conviction that the above principles, judiciously applied, will result in the decipherment of the ancient records of the Nahuas, such as that which is here presented, all who are conversant with the subject will acknowledge the propriety of calling to our aid the widest range of comparisons possible before proceeding to the interpretation of a particular manuscript. The mass of unexcelled material for this study which was originally collected by Boturini, and which through many perils is at last in a fair way to be rendered accessible to the scientific world, will add so much to our knowledge that it would be time lost to seek definite conclusions from the fragment here presented. The object of the Society which publishes it is accomplished when this testimony to a past culture is thus laid before the students of human development with such brief words of introduction.

# Part II.

## THE TRIBUTE ROLL OF MONTEZUMA.

BY HENRY PHILLIPS, JR.

The manuscripts here reproduced came into the possession of the American Philosophical Society in the year 1830, having been presented, together with about twenty-five hundred objects of Mexican antiquities, by Hon. Joel R. Poinsett, who had been Minister of the United States at Mexico.

The colored pictures will be found engraved [uncolored] in Lorenzana's Historia de Nueva* España, Mexico, 1770. They are numbered in that work respectively as 1, 2, 27, 28 and 30, and are designated as the catalog of the tributes paid to Montezuma, their amounts and species and the peoples by whom they were paid.

The tributes as paid consist of various manners of dresses, military and civil, arms, banners, etc., cotton, gums and spices, ornamented vestments and other articles, [even as it is said, lice and ants], precious stones, apparently *cut*, and necklaces of similar objects.

The pictures now presented will be found absolutely correct. Upon comparison with those in Lorenzana it will be seen that there are many discrepancies in form, shape, size and position; that in the printed volume some written matter is interpolated as explanations on the plates, and in other cases there are inscriptions omitted from the roll. The plates represent the tributes paid by Tlatelulco (Pl. 1), Tepetlaplalco (Pl. 2), Tlauhquitepec (27), Tuxpa (28), Tazco (30) and others.

# Part III.

## PHYSICAL AND ETHNOGRAPHICAL CHARACTERISTICS.

BY DR. J. CHESTON MORRIS.

The fragments of the tribute roll are four in number, those of the calendar, two. They are all of maguey paper, made from the fibre of the *Agave americana* by a very simple process: A section of the stem is shaved or cut so as to give a long thin strip which is macerated and rolled into the required density, texture, smoothness and thickness; in this case the width of the sheet was between eight and eight

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* Cordillera de los Pueblos que antes de la conquista pagaban tributo à el Emperador Muctezuma y en que especie y cantidad.

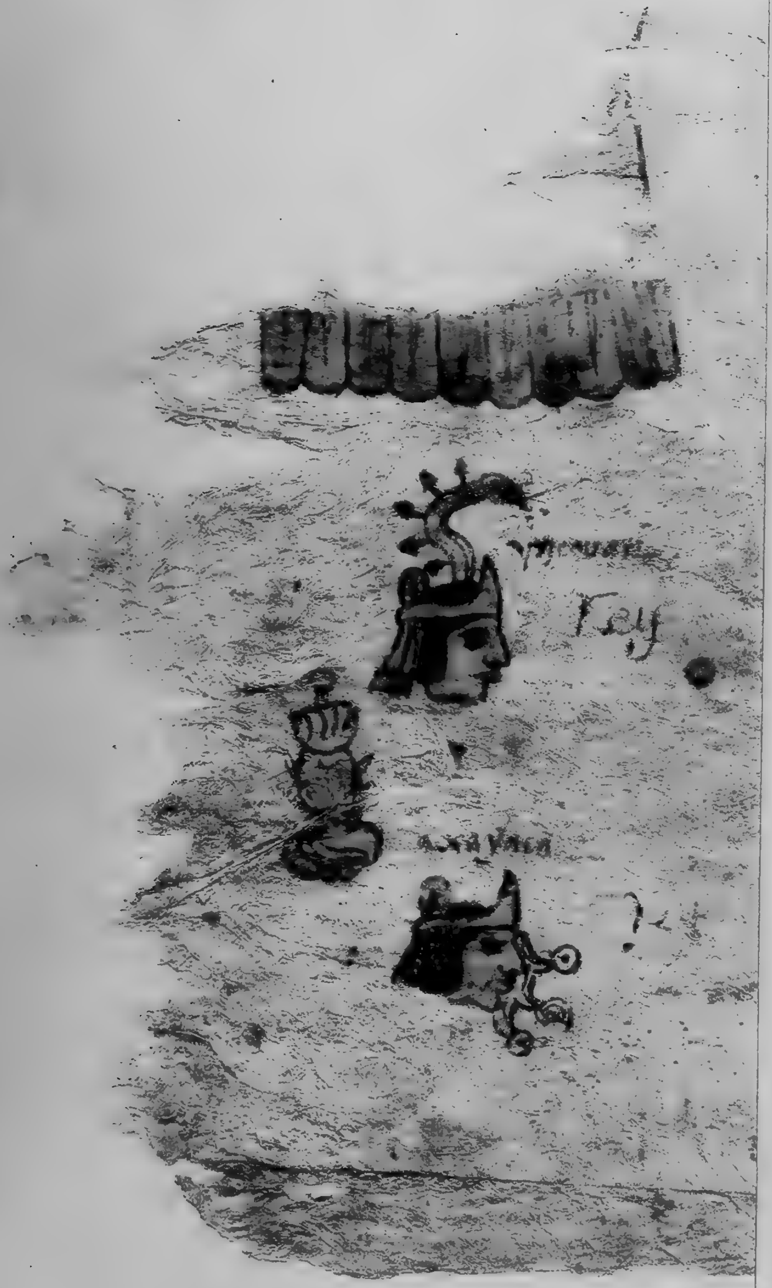
and a half inches. For the tribute roll a greater width was obtained by placing strips of two and a half inches wide on one side, while still moist, and causing them to be rolled or pressed into imperfect unity with the main strip; or, as in No. 4, by similarly uniting two sheets of full width and cutting off the edges. They then seem to have been cut into pages of seventeen inches long for the tribute roll. The outlines of all the figures have been carefully made with an ink resembling sepia, and then the various colors, probably of vegetable origin, filled in. These are shaded with much accuracy.

The ethnographic features of the pictures are very interesting and suggestive. Thus on No. 2, Tlatilulco, are four heads each surrounded with a very light yellow circlet rising into a point above, and fastened with a red bow or sash behind; the face is white with slight pink hue, the nose straight and pointed, eyes black, as also the long hair which covers the ears; the expression is that of command. Very different is the head on No. 30, near the foot of the page, the face of which is of a yellowish color, the hair represented as twisted in two coils which are intertwined around the head and terminate in horn-like projection above the rather high forehead, while the nose is aquiline, almost gibbous, with thick lips and prominent chin.

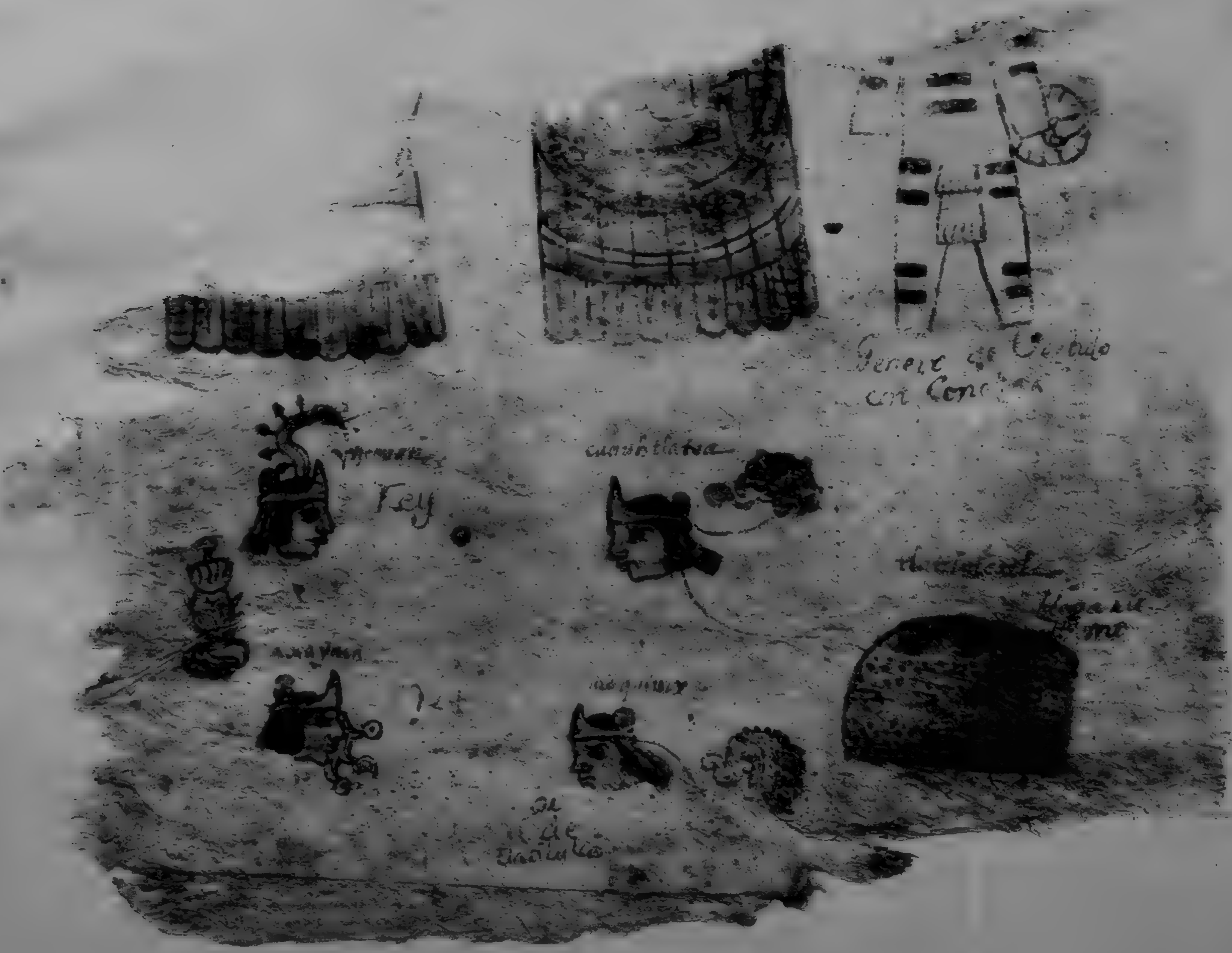
On the first of the two calendar sheets we see two heads without color, but surmounted by what may represent a cap or helmet with two horns; then a face which recalls in its outline those of the first fragment of the tribute roll. Then follow others, nearly all with very long straight noses, some of them however slightly gibbous. About midway on this sheet (which is forty-two inches long) is a representation of two square huts or houses, with roofs rising to a flat peak in the centre; in the line below that of a man seated in a curule chair, wearing a sombrero and plaited doublet, with a long straight sword held in front of his left hand. It would seem as though this were a narrative which was soon after abruptly terminated, as the illustrations above the circles which I take to stand for days are only three in number. It is worth noting that the faces are all turned in reverse directions in the alternate lines, thus making them advance first from left to right, and in the line below from right to left. The circles indicating days are usually ten in each row, sometimes eleven, once nine. Some bear a svastica symbol and are colored red; others at irregular intervals have a red face, with a gibbous pointed nose and very full lips, partly filling a white circle not concentric with the main one, which is otherwise always yellow. I believe these faces represent the phases of the moon.

The other calendar fragment, which is thirty-two inches long, is of inferior workmanship, has the day circles (some of which are colorless, others green and greenish yellow) arranged on the right side. On this again, near the lower end, is seen the Spaniard, with long thin features, seated in his curule chair and carrying his two-handed sword, while on the last line are represented three figures with hats having doubly curved rims and full bonnet-like crowns, the first seated in the curule chair holding the sword resting on its point; they all have thin beards, and the two others look as though advancing on a march of exploration.

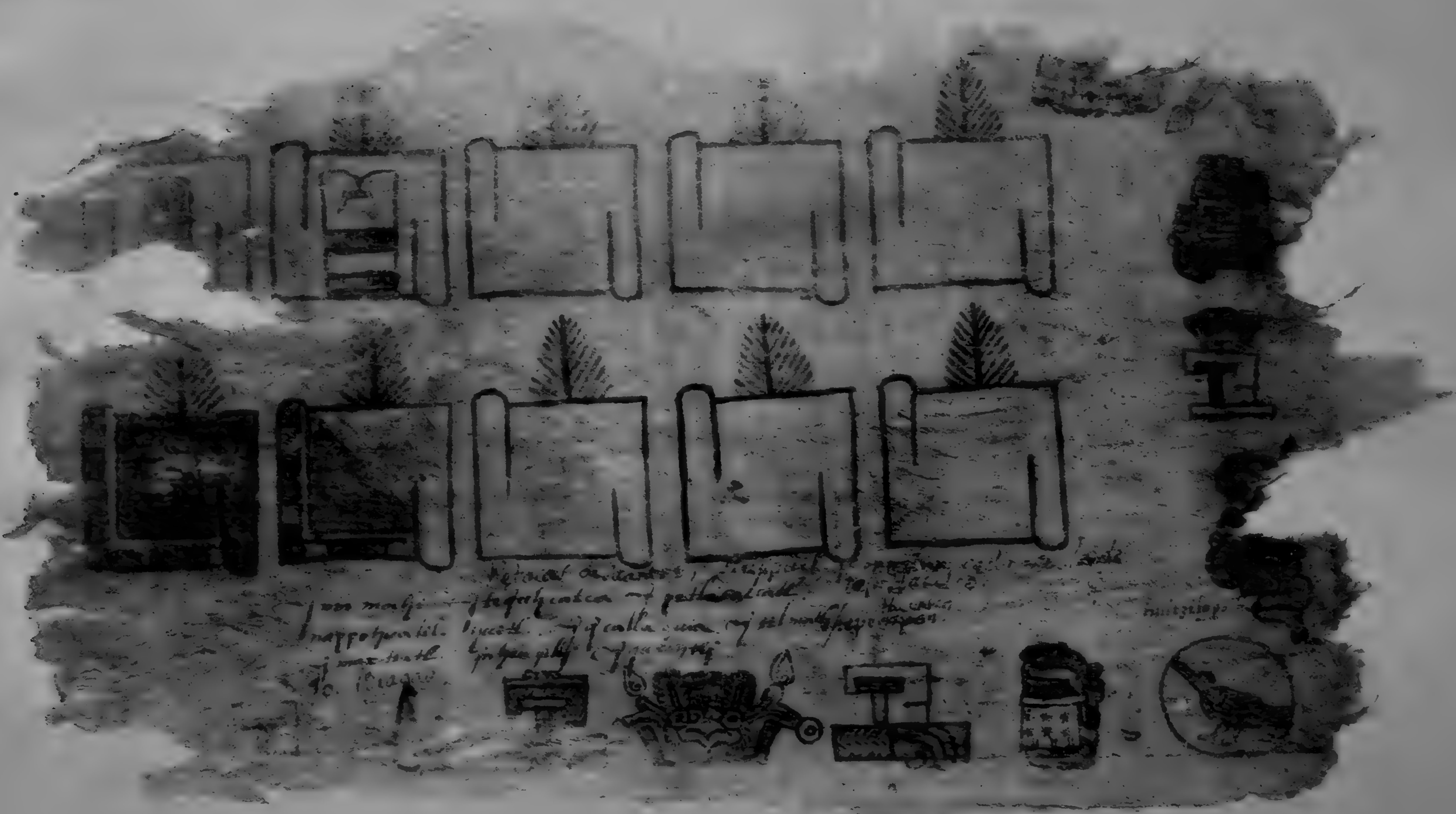
The Nahuatl words look as if made by a pencil, style, or short brush similar to that used in delineating the figures, and with a sepia-like preparation; while the Spanish ones have evidently been made with an ink containing iron, and an instrument which disturbed the gloss of the paper, as is shown by its penetration to fibres adjacent, giving the lines a sort of hazy margin occasionally.



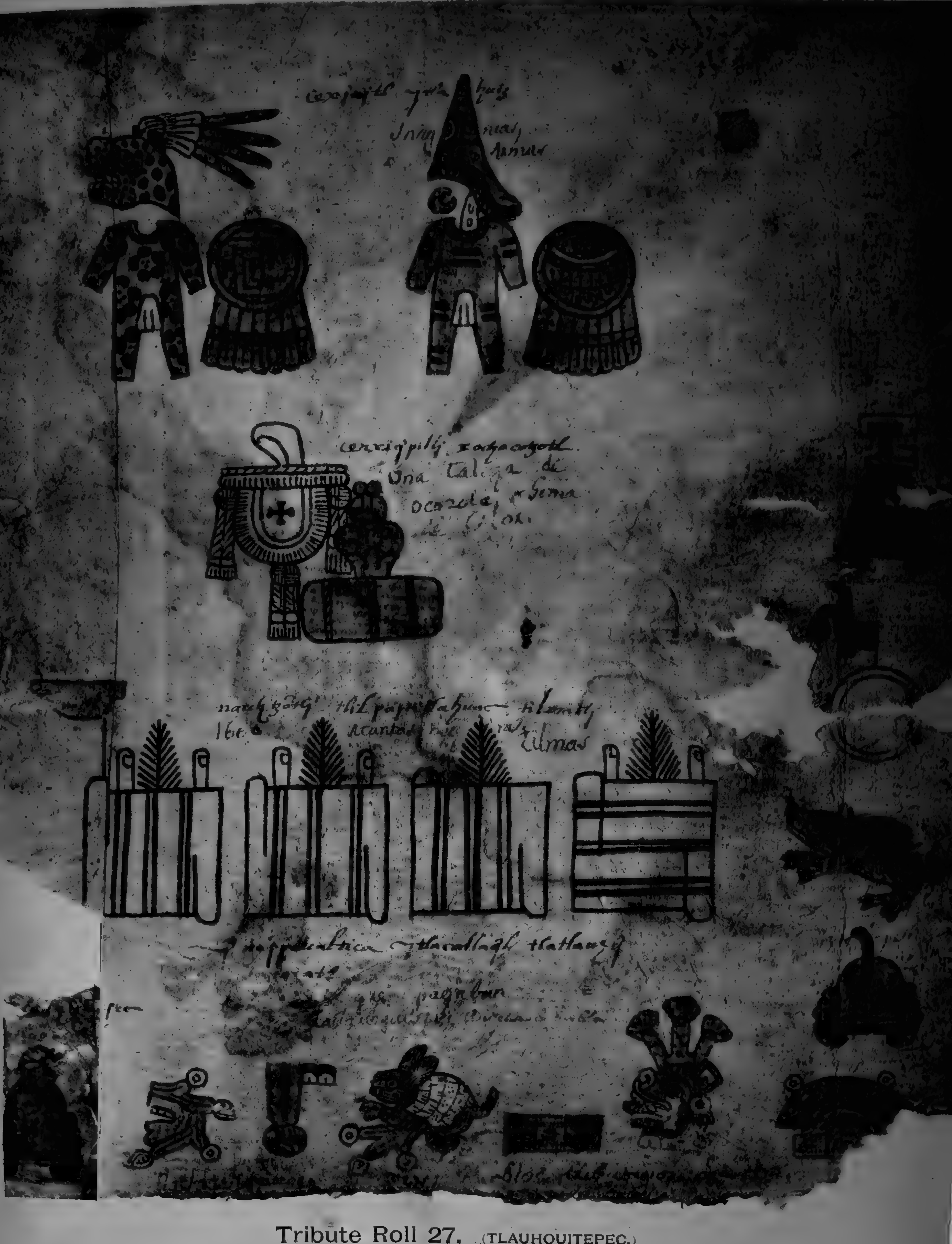
Tribute



Tribute Roll I. (TLATELULCO.)



Tribute Roll 2. (TEPETLATLALCO.)



Tribute Roll 27. (TLAUHQUITEPEC.)

Tribute Roll 30 (T47

Tribute Roll 30. (TAZCO.)

Tribute Roll 4. (CALENDAR I.)

Tribute Roll. CALENDAR 2.

# ARTICLE V.

# THE SAPROLEGNIACEÆ OF THE UNITED STATES, WITH NOTES ON OTHER SPECIES.

BY JAMES ELLIS HUMPHREY, SC.D.

**Read before the American Philosophical Society, November 18, 1892.**

In spite of the attention which most families of Thallophytes have received in the United States during recent years, the aquatic fungi have been hardly noticed. Although their resemblances to the Algæ on one hand, and to the Fungi on the other, give to their study peculiar interest, it is perhaps to this twofold affinity that the neglect is due. Their habitat is not such as is explored by the student of fungi, and the phycologist passes them by as not of his group.

The following pages contain the results of studies of American *Saprolegniaceæ*, carried on during the past two years in the intervals of other botanical work. The materials on which they are based have been largely procured by myself in and about Amherst, Mass.; but I have to thank the kindness of friends and correspondents in other parts of the country for considerable material illustrative of the Saprolegniaceous flora of their respective sections. Of these, I am indebted to Dr. Ida A. Keller, of Bryn Mawr College, for cultures from the neighborhood of Philadelphia, and for a single one from Kentucky; to Rev. A. B. Langlois, of St. Martinville, Louisiana, for cultures from that vicinity; to Prof. G. F. Atkinson, formerly of Auburn, Alabama, and to Mr. J. M. White, of Agricultural College, Mississippi, for specimens from those localities. I am also under especial obligations to Prof. William Trelease, of the Missouri Botanic Garden, at St. Louis, who has most generously placed in my hands without restriction all the preparations, notes and drawings made during his too brief study of the family, carried on chiefly in eastern Massachusetts in 1881. I am also indebted to Prof. Roland Thaxter, of Harvard University, for specimens from Mt. Washington; and I owe to Mr. A. B. Seymour, of Harvard University, references to the few published *exsiccatæ* of this family and the examination of one of them. The others I have not been able to examine.

While neither the amount of material examined, nor the variety of sources from which it has been drawn, can justify any generalizations, they yet afford a basis for some preliminary ideas concerning the distribution and relative abundance of some of our species. The material has also been utilized, in part, for the study of several questions relating to the morphology of the group, on which it is hoped to shed some light. Physiological questions have not received the attention which they deserve, and which it is hoped to give them in future studies. Their discussion is, therefore, restricted as much as possible in the present paper, which is concerned chiefly with the morphological and systematic aspects of the family.

A pretty careful review of the literature has led to some conclusions concerning the synonymy of certain species not yet known to be American which have not previously been suggested. Therefore, it has been thought worth while to include in the systematic account of the family all published names, with an indication of the standing of each, so far as it can be determined from available data.

The appended bibliography makes no pretensions to completeness, but it is believed to contain the titles of all works of present value, or of much historical interest, relating to the morphology and classification of the *Saprolegniaceæ*, as well as those of certain other papers which are quoted in the following pages. Papers by American authors are marked with a dagger (†). The titles of the few papers included which I have not been able to examine are preceded by an asterisk (*). For access to many of the remainder I am indebted to the various libraries in Amherst, Boston and Cambridge, and to Prof. W. G. Farlow, of Harvard University. Each of the works is cited in the body of the paper by its abbreviated date, which is prefixed to its full title in the list. This method has the advantage of doing away with cumbersome footnotes, and of giving, in the briefest possible form, the date of the work with the reference to it. The last point is one of much convenience and economy in the citation of synonymy.

## INTRODUCTORY.

The greater simplicity or apparent primitiveness of structure which is usually associated, among the simplest plants, with life in the water, together with the fact that various theoretical considerations point to the water as the probable habitat of the earliest forms of life, lends to the study of the aquatic Thallophytes the highest interest. Leaving out of consideration the natural and fairly circumscribed group of the *Schizophyta*, the great body of these forms is made up of plants containing chlorophyll, belonging to the algal stock, and presenting various lines of relationship and descent. From this stock must undoubtedly have been derived the great collateral chlorophyll-less groups of fungi. Most of the latter have been so modified to meet the conditions of aërial life, that the absence of chlorophyll has become of minor importance as a distinguishing character. A few, however, which cling to the ancestral habitat have preserved so many of the essential algal features that it becomes difficult to separate them from the *Algæ* except on the basis of their acquired saprophytic or parasitic habit and consequent loss of chlorophyll.

All of the characteristically aquatic groups of fungi belong to the most primitive or alga-like division—the *Phycomycetes*—and they are all probably to be regarded as primitively aquatic. Several interesting cases of transition from aquatic to aërial life are, however, presented by species immediately related to some aquatic ones and referrible to natural groups which may, in general, be called aquatic. The aquatic *Phycomycetes* may be grouped under five heads, as follows:

1. *Chytridiaceæ.*
2. *Ancylistaceæ.*
3. *Monoblepharidaceæ.*
4. *Saprolegniaceæ.*
5. *Pythium.*

The *Chytridiaceæ* constitute a heterogeneous group of considerable size and of much variety of structure. Its members are regarded by some writers as the most primitive of the fungi, and by others as degenerate forms derived from the higher *Phycomycetes.* They possess a very rudimentary mycelium or none at all, and commonly produce both sporangia, with zoöspores, and resting spores. An evident conjugation precedes the formation of resting spores in a very few cases; but, for the most part, the group presents no traces of sexuality. A considerable number of the species are parasitic upon terrestrial Phanerogams, usually such as grow in wet places; but the aquatic species constitute the larger part of the group and are also chiefly parasites. Their hosts include *Protozoa, Anguillulæ* and *Rotifera; Saprolegniaceæ, Algæ* of every group, various spores and pollen grains; in short, a large part of the minuter organisms of fresh waters, to which they are chiefly restricted. A few species, however, are marine.

The *Ancylistaceæ* include a few species, chiefly parasitic upon *Conjugatæ* and *Anguillulæ.* The young plant is mycelium-like, but is entirely consumed in the formation of the reproductive organs. These are sporangia, oögonia, and antheridia. From the union of the protoplasm of the last two, there results in each case a single oöspore. While clearly related in their vegetative structure and habits with the *Chytridiaceæ*, these plants may be regarded as forming, in their reproductive organs, a transition to the higher *Oömycetes.*

The *Saprolegniaceæ* are to be discussed later.

Closely related to them, but differing in essential particulars, is the single genus *Monoblepharis* which forms the type of a distinct family. It has been studied only by Cornu, who has described three species. According to this author, the plants have sporangia with uniciliate zoöspores; and the oöspheres, formed singly in the oögonia, are fertilized by motile uniciliate antherozoids, produced in a cell cut off just below the oögonium from its supporting filament, which gains access to the oösphere through an opening at the apex of the oögonium. These plants are saprophytes.

The *Peronosporaceæ* are represented among aquatic fungi by some of the members of a single genus, *Pythium.* Like the rest of the family, the members of this genus have an abundant mycelium from which are developed the sexual organs, antheridia and oögonia. Each of the latter produces a single oösphere from a portion of its protoplasm, the rest remaining as "periplasm," and ultimately forming an outer coat about the spore. There appears to be an actual passage of protoplasmic substance from the antheridium to the oösphere, constituting a real act of fertilization. In *Pythium*, as in some of the *Ancylistaceæ,* the zoöspores are formed outside of the mouth of the sporangium from the contents of the latter, after it has been extruded in a single mass. The aquatic species of the genus are parasitic on water plants or saprophytic on organic remains. One or more species attack terrestrial Phanerogams.

The American literature of these various groups is confined to a few scattered notes in addition to that quoted in the present paper, with the exception of Prof. Farlow's account of the genus *Synchytrium* of the *Chytridiaceæ.* Its members are, however, not aquatic.

This brief preliminary account may suffice to indicate the near relationship of all the aquatic fungi and to suggest the great morphological interest which attaches to them; while it may suitably preface the detailed discussion of the family which forms the subject of the present contribution.

## SAPROLEGNIACEÆ.

The vegetative organs of these plants consist of usually branched tubular filaments without dividing walls, and therefore with a single continuous cavity. The filaments are of two sorts—the internal threads, which penetrate the substratum, branching freely, and tapering rapidly to their pointed ends (Fig. 2), and the external ones, which arise from the latter and radiate outward into the surrounding medium (Fig. 1). The following description refers chiefly to the latter.

In general, there are no sudden changes in the calibre of a filament, but only a gradual decrease from one end to the other; but the *Leptomiteæ* are characterized by abrupt constrictions at intervals, marking off the hyphæ into segments, but not completely closing the cavity (Fig. 6). The hyphæ are usually largest at their bases; that is, where they arise from or give rise to threads of the other kind. From this point the external threads decrease slowly in size. Those of *Leptomitus*, however, decrease abruptly with each successive branching, so that their apical segments become reduced to an eighth of the diameter of the basal ones. The different species present very wide extremes in the size of their filaments, whose diameter may vary from $5\mu$ in *Aphanomyces* to more than $100\mu$ in *S. Treleaseana.* The length of the filaments in any given species or individual is considerably affected by the amount of available nourishment; but in vigorous specimens of *Aphanomyces* it may not exceed two or three millimeters, while in some *Achlyæ* it may reach more than twenty millimeters.

The hyphal walls of the members of this family are composed, unlike those of almost all other fungi, of unmodified cellulose, which reacts readily and characteristically with chloroiodide of zinc. Within this wall is a layer of protoplasm which lines it closely and forms a hollow cylinder. At the centre is a wide vacuolar space, across which run, especially in the younger parts of the filament, strings of protoplasm connecting opposite parts of the parietal layer. This layer is densest and most granular in the youngest or apical part of the filament, and in the older parts the granular protoplasm forms a network of anastomosing threads or bands, with somewhat wide interstices (Fig. 4). In the threads of this network a constant circulation is kept up, towards the base in some and towards the apex of the hypha in others. It is worthy of remark that when young threads are cut off in water their death does not necessarily result. Very little protoplasm is lost from the tube thus opened, but a new cellulose wall is very quickly formed across the cut end (Fig. 3), and the hypha remains capable of normal development if nourishment be again supplied, or even of developing until its protoplasm is exhausted, without further nourishment.

Scattered through the protoplasm without order, but commonest at the nodes of the granular network, are the nuclei, normally ellipsoidal in form, and each with a distinct central mass which stains more deeply than the rest of the nucleus (Fig. 4). These central masses have been generally termed nucleoli, but they seem clearly to correspond rather with the chromatin bodies of more highly organized nuclei, and will, therefore, be better designated as chromatin-masses. Between the chromatin-mass and the nuclear membrane is a considerable space occupied by a substance which stains very slightly with hæmatoxylin. The nuclei are most abundant in the young parts of the hypha, where the protoplasm is densest. They increase in number, with the apical growth of the thread, by fission. The division of the nucleus is preceded by the division of the chromatin-mass, and commonly occurs in a plane at right angles to its long axis (Fig. 5). I have observed some cases, like one shown in Fig. 4, where two nuclei lie close together, with their long axes parallel, but have never seen preliminary stages to convince me that they have resulted from the division of a nucleus in the plane of its long axis. Hartog states ('89) that he has observed karyokinetic phenomena in some cases, but I have been unable to find evidence of any other than direct division.

The growth of the hyphæ takes place at their blunt or somewhat pointed tips. Data as to the rate of growth are very few. Pringsheim ('51) reports a rate of 400$\mu$ (= .4 mm.) per hour in a new filament of *Saprolegnia*, growing into an emptied sporangium. Hine ('78) records having observed a growth of 70 to 90$\mu$ per hour during three hours' observation of a filament of *Saprolegnia;* and I have measured a growth of about 100$\mu$ per hour in a vigorous hypha of *Aphanomyces*, while the germ-tube from a zoöspore of the same species grew at the rate of about 40$\mu$ per hour in water.

The purely vegetative branching of the hyphæ is sometimes dichotomous at the principal divisions of the larger ones, but commonly of the monopodial type in the small branches. In most species the branches may arise from any point and develop by apical growth at acute or right angles with the main axis. In the genus *Leptomitus*, as here limited, branches arise only from the acroscopic ends of the segments, close to the origins of the next segments of the axial series (Fig. 6). They are separated by constrictions from their parent segments; but when the segment next below a sporangium gives rise to a branch, it grows out for a short distance without constriction, and then produces a new segment (Fig. 116), as Pringsheim has pointed out ('60).

The internal hyphæ, whose office is the absorption of nourishment from the substratum, may properly be termed *rhizoids*, whether from a morphological or a physiological point of view. DeBary states ('81, p. 95) that the external hyphæ may send down rhizoidal branches which penetrate the substratum. Well-developed threads, when cut off from their basal portions and brought in contact with fresh nourishment, will attach themselves to it by new rhizoids and continue their growth.

In addition to the protoplasmic contents and the food material diffused through it, the hyphæ of the *Saprolegniaceæ* contain more or less generally certain bodies as yet unrecognized in other plants. They have been called by Pringsheim ('83 *b*), cellulin granules (Fig. 6, *c*). They occur in the filaments or in reproductive organs formed from them, as discoid or lobed bodies, those of the latter form arising by fusion of several disks. When young, they are homogeneous and rather strongly refractive; and when old they often become distinctly stratified. They are, perhaps, most abundant and conspicuous in *Leptomitus lacteus*, where they were early described by Pringsheim ('60) as nuclei. In this species they often become lodged in the constrictions of the hyphæ and may completely close the passage. Pringsheim has shown ('83 *b*), that the substance of these bodies is neither a proteid nor a carbohydrate, although it is in some respects related to cellulose and starch. He regarded them as waste products of metabolism rather than as reserve materials, since he saw no evidence of their solution or transformation. But Rothert has shown ('88) that they probably contribute to the formation of the separating wall of the sporangium, since they seem to disappear during that process. It may also be suggested that cut hyphæ may owe their power of promptly repairing injury to the presence of this material. Should this be shown to be the case, they may be regarded as a soluble form of cellulose available for use in forming and repairing cellulose walls.

## Non-sexual Reproduction.

After they have become well grown, the external hyphæ begin to produce the organs of reproduction, which are of two sorts, sexual and non-sexual. We will consider these as they are developed in the order of time, examining first those of non-sexual or vegetative reproduction. Only a single organ of this sort is common to the entire family; namely, the *zoösporangium.* Within this organ are produced the agents of the rapid propagation of the species concerned, the *zoöspores.* The phenomena of the development and individualization of the zoöspores within the sporangium appear to be essentially the same in most of the genera, at least. But the manner of their release from the sporangium and their subsequent history undergo various modifications so characteristic and so related to each other that they furnish the basis for the grouping of the species into a natural series of genera. We pass to a detailed examination of their production and fate.

The first account to give an approximately correct description of these phenomena was that of Hannover ('42), followed by that of Unger ('43). Subsequently Pringsheim ('51) and DeBary ('52) extended their observations, and the subject has been a favorite one down to the present. The formation of a sporangium begins with the gradual cessation of the apical growth of a filament. Now commences an accumulation of protoplasm in the terminal portion of the filament, which usually becomes more or less swollen. No increase in size occurs, however, in the hyphæ of *Aphanomyces*. Finally the end of the hypha is filled with a very dense mass of protoplasm with numerous nuclei, which passes rather abruptly into the thin protoplasm of the lower part. In the narrow intermediate region between the dense and the thin protoplasm, is formed a clear disk of hyaloplasm, seen as a band in lateral view. Its hyaline character is due to the withdrawal of the microsomes from the originally granular protoplasm of that region. Across the lower surface of this disk is developed a cellulose wall, beginning at the wall of the hypha as a ring and progressing rapidly inward from all sides until the central opening is closed, and a solid wall separates the terminal portion of the thread, as a sporangium, from the remainder. It has been said that this basal wall of the sporangium is different chemically from the other cell walls of the plant. Not only is this improbable *a priori*, especially in view of its common fate in *Saprolegnia*, but careful examination shows that it reacts like the other walls with chloroiodide of zinc. As before remarked, Rothert ('88) has observed the occurrence of abundant cellulin granules in the region of the forming wall. Later these cannot be recognized and he suggests that they may furnish material for the wall. The hyaloplasm which thus at first lines the sporangial surface of this wall soon becomes again granular by the return of its microsomes.

The sporangium thus formed was regarded by earlier writers—Naegeli ('47) and others—as a free cell enclosed in the end of the filament. It differs widely in form in the different species, and even considerably in the same species. Commonly it is approximately cylindrical, and may be swollen most at its apical end (*Saprolegnia*), or in the middle (*Achlya*), with a length from six to twelve times its greatest diameter. In *Pythiopsis*, *Thraustotheca* and *Apodachlya pyrifera*, the length is so reduced that it becomes short-clavate or pyriform; and in some sporangia of *Pythiopsis* and in *Apodachlya brachynema*, the form is quite globular. These contracted forms occur also among more typical ones in *S. torulosa*. On the other hand, the sporangia of *Aphanomyces* often reach a length of more than a hundred times their diameter.

In rare cases, the quantity of protoplasm contained in the sporangium may be sufficient to completely fill it, but usually it forms a parietal layer of greater or less thickness, with a vacuolar space extending through the middle. If this layer be very thin, or if the sporangium be completely filled, that condition will induce certain modifications in the usual course of development of the zoöspores, but in a great majority of cases the process is as follows. In consequence of the greater turgidity of the sporangium than of the lower part of its hypha, its basal wall becomes convex towards the base of the filament (Fig. 7, *a*). The first indications of the formation of zoöspores then soon follow. The phenomena attending this process have been the subject of much study and of widely different interpretations, most of which cannot profitably be detailed here. The most important contributions to the discussion have been those by Strasburger ('80), Büsgen ('82), Ward ('83), Berthold ('86), Hartog ('87), and Rothert ('88); and their papers may be consulted for the details of the various views put forth. Repeated studies of several species have satisfied me that Rothert's account, which is corroborated in most details by Berthold and Hartog, is practically correct. Therefore the following account is a combination of the descriptions given by those writers with personal observations. The description may best be based, as has been said, on the commonest form of sporangium, that with a parietal layer of protoplasm of considerable thickness and an axial vacuole. At first, irregular rifts begin to appear in the protoplasm, extending outward from the vacuole. They soon become more definite and more numerous, and connect with each other in such fashion that the protoplasm is marked off into a number of irregularly polygonal masses, as seen from the surface (Fig. 7, *a*). It is probable that the number of these blocks, which finally become spores, corresponds to the number of nuclei originally shut in by the basal wall, since the zoöspores are always uninucleate, and there is no evidence that any nuclear division occurs within the sporangium. The clefts are at first quite narrow, and the protoplasmic masses, or "spore origins," as they have been called, are frequently connected by threads of protoplasm. The somewhat irregular outlines and the granular structure of the origins, together with the appearance of the connecting threads in surface view, have led Strasburger, Büsgen and Ward to very different interpretations of these clefts from those here adopted. They have regarded them as "cell-plates," separating the spores, and consisting of layers—lines in optical section—of granules. But it is clear that Rothert's explanation is the correct one, since, as the clefts broaden, the granules disappear, or separate with the origins.

At about the same time, with the appearance of the first signs of the segregation of the spore origins, there is formed, if the sporangium belong to a species of *Achlya* or *Saprolegnia*, normally at its apex, an outgrowth or papilla, from whose tip the zoöspores will finally escape. Its formation begins with the accumulation at that point of a mass of hyaloplasm which presses the wall outward. After its formation, the hyaloplasm becomes granular, except a thin layer which remains intimately connected with the apex of the papilla (Fig. 7, *a*). This apical wall is always less sharply defined and more highly refractive than any other part of the sporangial wall, and these characteristics become more and more prominent until the escape of the spores.

The clefts between the spore origins rapidly widen and deepen, causing the connecting threads to become broken and withdrawn into the bodies of the origins. In view of subsequent changes, and of what seems the most reasonable explanation of them, it does not appear probable that the clefts extend at once completely to the outer wall, although it is often very difficult or even impossible to detect with high powers and excellent material any protoplasmic lining of the wall at this stage, when the spore origins are most widely separated. Another good reason for believing that the origins are still connected by a delicate parietal lining may be found in the fact that the whole surface of an origin next to the wall remains closely applied to it throughout this stage, and does not become rounded off at the corners, as happens on the other sides of the origin, and on this side at a later stage.

After the separation of the spore origins has become nearly complete, there follows suddenly and without warning the so-called "homogeneous" stage of Büsgen, the "stage of swelling of the spores" of Rothert. The spaces between the spore origins disappear by the apparent swelling up and fusion of the separate origins, and the contents of the sporangium appear less opaque and less granular than before. In spots corresponding approximately to the middles of the spore origins are to be seen clear, bright spots, and throughout the whole protoplasm are numerous vacuoles which appear and disappear, shifting about rapidly (Fig. 7, *b*). At the same time with the beginning of this stage, there is a very sudden decrease of turgidity in the sporangium, which is shown by the flattening of the terminal wall of the apical papilla, previously convex outward, and by a complete change in position of the basal wall (Fig. 7, *b*). This wall has been until now, as before stated, convex downward, on account of the greater turgidity of the sporangium than of the lower part of its hypha. These relations evidently now become reversed, for the wall suddenly becomes convex upward, indicating a marked and instantaneous loss of turgescence by the sporangium. All the characteristic phenomena of this stage are much more strongly marked in the species of *Achlya* (*A. Americana* and *racemosa*) than in those of *Saprolegnia* (*S. ferax* and sp. indet.) which I have studied. The change may come over a whole sporangium simultaneously, so far as the eye can detect, or it may begin at either end and extend, wavelike, to the other in two or three seconds. While the spore origins seem ordinarily to be quite fused together, careful examination will not seldom show, here and there in the protoplasm, narrow cracks which are the remnants of separating clefts not quite completely closed by the swelling of the origins. Rothert's explanation of this phenomenon seems to accord well with the observed facts and with what we know of cell structure in general. He believes that, until the beginning of the stage of swelling, the sporangium wall is lined by a continuous protoplasmic layer, and therefore, as in living cells generally, there can be no transfer of liquids between the cavity of the sporangium and the surrounding water. The final extension of some of the dividing clefts between the origins to the wall breaks the continuity of this "primordial utricle," and there is an escape of fluid through the pervious wall and a consequent loss of turgidity. This fluid is distinctly attractive to some forms of Bacteria which may be present in the surrounding water and is, doubtless, the cell sap. Its loss is due, Rothert thinks, to the contraction of the walls which have been distended by their dense lining, but now become free to assume their natural positions. Measurements show a reduction in the volume of the sporangium amounting in some cases to as much as thirteen per cent. After this loss, water is probably taken up by endosmose, and the mixture of cell sap and water in the cavity of the sporangium is absorbed by the spore origins, whose bulk is so increased that the separating spaces are practically obliterated. The successive absorption and expulsion of this fluid gives rise to the shifting vacuoles. My observation that sometimes in *S. ferax* the swelling of the spore origins begins perceptibly later than the incurving of the basal wall, distinctly corroborates this view.

A very few minutes after the swelling up of the origins, the vacuoles disappear, and the granular appearance returns. They begin again to contract, separating from each other on the old lines, as consecutive observation always shows. The contraction goes on rather rapidly, and the masses become definitely separated as independent spores. While this contraction is going on, small portions of protoplasm may become cut off from the different spores; but each is soon taken up, as a rule, by the same spore to which it originally belonged. The significance of this phenomenon will be discussed in connection with the sexual spores, during whose formation it also occurs. The gaps between the spores are widened by their contraction and the rounding of all their corners so that they come to lie nearly or quite free from one another. In *Achlya racemosa*, and perhaps in some other species, the contraction is much less pronounced than is usual, and its spores do not commonly appear distinctly separate in the sporangium.

Up to this point our account may apply equally to all the species that have been carefully studied. But we must now distinguish between those genera whose spores normally escape from the apex of the sporangium and those of which this is not true. In those of the former class (*Achlya*, *Saprolegnia*, and allied genera), there may often be seen some spontaneous movement among the spores, especially among those near the tip. In case of the two genera just named, the apical papilla becomes markedly more transparent and less sharply outlined, as to its terminal wall. As the spores acquire more exactly their ultimate form, the motion increases and the terminal wall fades out until it is ruptured, and the spores rush through the opening (Fig. 8). Sometimes the wall seems to soften gradually until it yields to pressure from within; or again, the spore nearest the apex may be seen to enter the papilla and apparently to force its way through the partly softened wall, thus making an opening through which the rest rapidly follow. Other modes by which the opening is made have been detailed by Rothert ('88), but need not be further discussed here.

Some figures concerning the rapidity of the development of the zoöspores have been given by others, and I have made notes of the process in the four species chiefly studied. Ward ('83) gives some observations on *A. De Baryana* ("*polyandra*") and *A. apiculata*, and these accord with my own on *A. Americana* and *racemosa* as closely as could be expected. There is considerable variation in the time occupied, depending on the age and vigor of the culture, and doubtless on various undetermined conditions. A general statement may, however, be based on the data at hand. The first appearance of the clefts, which mark the beginning of the formation of the zoöspores, usually occurs twenty or thirty minutes after formation of the basal wall. From their appearance to the escape of the zoöspores the time may be from twenty-five minutes to an hour, but it rarely exceeds forty-five minutes. The emptying of the sporangium is ordinarily accomplished in from forty-five to one hundred seconds.

The zoöspores are ovate or pyriform, and their protoplasm is hyaline at the smaller end, while in the rest of the spore it is very granular, and contains two or three contractile vacuoles (Fig. 8, *z*, and 9). The zoöspores of the species of *Saprolegnia* (Fig. 8, *z*) and *Pythiopsis* (Fig. 63, *z*), and of some, probably of all, species of *Achlya* (Fig. 9) are provided with two cilia attached to the smaller, hyaline end of each. The presence of these organs in the first-named genus has been recognized since they were demonstrated by Thuret ('50), but Cornu was the first ('72) to assert their presence in *Achlya*. Hartog ('87) later corroborated his statement for *A. polyandra* and *recurva*. I have several times recognized cilia on the zoöspores of *A. Americana*, at the instant of escape, by adding to the water on the slide supporting the specimen a few drops of a one per cent. solution of osmic acid in water, and then staining *in situ* with a solution of equal parts fuchsin and methyl violet in strong alcohol. This treatment, recommended by me ('91) in a previous note on the subject, demonstrates the presence of cilia unmistakably. In an exceptionally favorable specimen of *A. Americana* I have seen the cilia on the living zoöspores, both before and after their escape from the sporangium; and in *A. polyandra* one can hardly fail to notice the very marked ciliary motion within the sporangium during the escape of the spores. It is not improbable that the zoöspores of *Aphanomyces* are also ciliate, but this has not been shown, and the genus needs more careful study than it has yet received.

Sometimes the spores escape with the ciliate end directed forward, but it appears to be much more usual for them to pass out in the reverse position. The first spores to leave do so very rapidly, and are closely crowded together, as though strongly impelled from behind or attracted from before. In the species of *Achlya* all the spores press outward in a close column, but in *Saprolegnia* there is a gradual decrease in the rapidity of their escape, and the last spores may linger for some seconds or even minutes, swimming aimlessly about, and sometimes never finding the exit.

The zoöspores of *Saprolegnia*, *Leptolegnia*, *Pythiopsis* and *Leptomitus* escape separately into the water, and swim about freely by means of their forward-pointed cilia. After a short time, varying from a few seconds to fifteen minutes, each spore ceases to move about, but continues for a time longer to whirl and rotate, assuming meanwhile a spherical form. Sometimes a few whirls are followed by complete quiet, but often the spore continues to struggle for ten minutes or more, as if in vigorous protest against giving up its activity.* Finally, it becomes quite spherical and motionless, though the cilia may occasionally be seen to wave slowly for a time longer, and then to disappear by degrees, being apparently withdrawn into the protoplasmic mass. The spore now becomes encysted by the secretion of a cellulose wall, and so, for the first time, constitutes a closed cell. Huxley has stated ('82) that the spores

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* A curious phenomenon, calculated to arouse speculation as to the nature of the changes of relations and tensions which take place while the zoöspore is coming to rest, has been observed by me in a spore of an undetermined *Saprolegnia*. After swarming normally, the spore had nearly come to rest, though with prolonged and vigorous struggles, when suddenly it burst with much force, scattering most of the granular protoplasm to a considerable distance, and leaving where it had been the nucleus with a small part of the protoplasm. There was, as yet, no trace of a membrane.

of the *Saprolegnia* of the salmon disease become motionless and encyst without swarming on leaving the sporangium.

The zoöspores of *Achlya*, *Aphanomyces* and *Apodachlya* only reach the water just outside of the sporangium, and there become encysted, each one, as it leaves the mouth, slipping into its place and rounding off at once, so that all the spores from a sporangium form a hollow sphere or hemisphere, into which the tip of the sporangium projects slightly (Figs. 10, 11). In other words, their cilia serve to carry the spores only through the mouth of the sporangium. In *Achlya* the escaping spores form a column so compact that considerable space is left between it and the wall, and they cling closely together during the entire emptying of the sporangium. It is always noticeable that the spores in this column keep their long axes parallel with each other. In *Aphanomyces*, each of whose sporangia produces but a single file of zoöspores, the spores are compelled by the narrow space in which they are formed to take a cylindrical shape. They pass in slow succession down to the mouth, and there become encysted (Fig. 11). There is no crowding or clinging together, and the complete emptying of the sporangium requires a much longer time than in the genera already described.

Hartog attributes this encystment of the spores at the mouth of the sporangium to a mutual attraction between them which he terms *adelphotaxy*, and which is also shown in their pressing closely together during their escape, in *Achlya*. It may well be that in *Aphanomyces* they are prevented by their narrow quarters from showing the same peculiarity inside of the sporangium. If we accept the existence of such an attraction, we must believe that it is stronger than the power of the cilia to carry the spores apart, or else that it is concomitant with a very transient development of cilia. In the present state of our knowledge some assumption is necessary to account for the phenomena which have been described. The spores are held together by no material connections, and, at least in some species, are provided with cilia. That these phenomena are dependent upon the life of the spore is shown by the fact that, if a solution of osmic acid, which instantly kills and fixes the spores, be added at the moment of escape, not only is their accumulation into a sphere stopped, but they are freely separated and carried about by diffusion currents in the surrounding liquid. It is hardly necessary to add that osmic acid would so harden any accompanying mucus from the sporangium that the spores would be held firmly fixed if such substance were present, as some writers have believed. Hartog's assumption of a mutual attraction between the spores seems as little open to objection as any that can be suggested, and should be so stated as to include a tendency to place their long axes parallel. This tendency, combined with the effort to secure as much exposure as possible to the surrounding medium, may account for their arranging themselves in a hollow sphere.

We may ask here what causes lead to the emptying of the sporangium. The existence of a special expulsive substance which swells strongly on absorbing water was assumed by earlier writers, Strasburger ('80), Büsgen ('82) and DeBary ('84). It was believed that the supposed "cell plates" of the first separation stage swell into an intermediate substance enclosing the spores and expelling them by its rapid and enormous increase in volume when water enters the sporangium. But the existence of this hypothetical substance has been sufficiently disproved along with that of the "cell plates." The only species in which an intermediate substance appears to exist is one in which it could be of no service in expelling the spores, as will be seen later; namely, *Thraustotheca clavata.* Since this species was the one which Büsgen studied in most detail, the reason for some of his views becomes evident. In general, there can be little doubt that the spores of the genera now under discussion leave the sporangia automatically. The preliminary changes in the wall, normally at the apex of the sporangium, which render the escape of the spores possible, involve interesting physiological questions which will not be discussed at present. But the nature of the stimulus which causes the spores to avail themselves as quickly as possible of the means of escape provided, may be briefly discussed. It frequently happens in *Achlya* and *Saprolegnia* that the spores do not leave a sporangium which has opened normally, but become encysted within its interior. This failure to leave the sporangium must evidently be due to the absence of the usual stimulus. Hartog ('87), and before him Cornu ('77), has held that the presence of free oxygen in the water is the determining factor. Rothert ('88) disputes this view, as well as Hartog's statement that such sporangia appear chiefly in poorly aerated cultures. And Hartog has more recently ('88) suggested that the spores may vacate the sporangium to find purer conditions than prevail within it; in other words, to escape from the products of their own metabolism.

In the first place, it may be remarked that it is much less probable that the hereditary phenomena of spore development within the sporangium should vary than that differences should occur in the external conditions of different cultures, or of the same culture at different times. Since there is no evidence that the formation of the spores presents any abnormality in those sporangia which fail to discharge their contents, we cannot suppose that the need of purer conditions exists less in one sporangium than in another. But some sporangia with normally developed mouths fail to discharge their spores when others are wholly emptied, though it is more common to find most of the sporangia formed at a given time in the same condition in this respect. This points strongly to some attractive and variable constituent of the surrounding medium as the cause of the normal exit of the spores.* The aimless wandering and frequent failure to escape of the last few spores in a *Saprolegnia* sporangium may be attributed to the fact that the water from outside has so far filled the sporangium that the difference between the media within and without the sporangium has become practically neutralized by their mingling. That the attractive force is normally very strong is shown by the following observation. A sporangium of *Achlya Americana* had developed abnormally three escape papillæ, one near the apex, one near the basal wall, and one midway between the others, all on the same side. The middle mouth was the first to open, and the spores rushed out in normal fashion until about a third of them had escaped. Then the other two mouths opened almost simultaneously, and the spores nearest them broke away from the column of which they formed a part, and crowded out through the new openings. Thus the force causing their exit was stronger than their tendency to cling together, and drew those within its range away from the main body. Whether the attraction is due wholly to the presence of free oxygen seems still open to doubt, although Hartog's experiments ('88) show it to be a factor of prime importance. It is true that failures of the sporangia to empty normally occur often in old cultures in which the oxygen may well be largely exhausted, and very often in cultures which have become overrun by Bacteria, Infusoria, and other foreign organisms. But cases occur which do not seem explicable on this basis alone. For example, in cultures on the slide with a comparatively small quantity of water, though quite sufficient for the swarming of zoöspores, sporangia often fail to become emptied, yet here there can be no suspicion of any lack of oxygen, but rather an unusual abundance of it.

In spite of the great differences in the size of the sporangia in different species of *Saprolegniaceæ*, and even in the same species, the size of the zoöspores, as measured after their encystment, varies but little, except in *S. anisospora*, which is not yet known to be American. The encysted spores are quite exactly spherical in all the American species studied, and are almost always between 8 and 12$\mu$ in diameter. Those of a given species may show a tendency toward one or the other of these extremes, but they present no constant characters in this respect, and are of absolutely no diagnostic value. Each spore contains a single nucleus, one of the original nuclei of the sporangium, of a nearly globular form, but otherwise like those of the

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* On the other hand, the mouths of some *Saprolegnia* sporangia often resemble very exactly the opening formed in a glass tube with one closed end, by forcing air into the open end while a small area on the wall is softened in a flame. The likeness is so striking as to suggest at once the action of an impulsive force from within the sporangium (see Fig. 50).

growing filaments (Fig. 12). The number of spores formed in a sporangium depends, then, on its size and the thickness of its protoplasmic lining. In an undetermined species of *Saprolegnia* I have estimated as nearly as possible the number of zoöspores produced in each of two sporangia of different sizes, with protoplasm of about average thickness. One $270\mu$ long by $26\mu$ in average diameter gave rise to about 120 spores, while from one $373 \times 32\mu$ about 250 spores escaped. A comparison shows that the volumes of these two sporangia bear almost precisely the same relation to each other as the numbers of zoöspores formed in them.

After remaining encysted for a few hours, the zoöspore begins to show renewed activity. A small, circular perforation is made in the enclosing wall, and the contents begin to emerge in the form of a small papilla, which gradually enlarges until finally the entire protoplasmic mass lies outside of the cast-off membrane (Fig. 11). The mass soon takes the form of a biciliate zoöspore, and after some preliminary efforts, darts away and swims freely about. In this second active stage the spore has exchanged its original form for that of a kidney bean, its cilia being attached at the lateral depression which corresponds to the hilum of the bean (Fig. 11, *z'*). At the point of attachment the protoplasm is, as in the first form, hyaline. The cilia are of unequal length, and the shorter is directed forward, the other backward, during the swarming. It is an interesting fact that this form of the zoöspore corresponds with those of the related *Peronosporaceæ*, and with those of some of the *Ancylistaceæ*. It would seem that this must be regarded as the primitive zoöspore of the *Phycomycetes*, as Ward has suggested ('83), the form with apical cilia being a secondary one acquired within the limits of the present family. After half an hour or more of activity, the spore again settles down and becomes encysted as before.

In most of the genera now under discussion, this double swarming or *diplanetism* of the zoöspores is the rule, although in exceptional spores the second swarming may be omitted without apparent influence upon their germinating power (Fig. 11, *a*). It would seem that the object of the first swarming is the emptying of the sporangium, and that of the second the distribution of the spores, to enable them to reach new sources of food supply; since, as Pfeffer ('84) has shown, they are strongly attracted by various organic substances. Although the first swarming accomplishes both ends to a considerable degree in *Saprolegnia*, it does not permit the wide distribution which the longer second period allows. The zoöspores of the second form also seem to range over a much wider region and to be more actively locomotive than those of the first. The condition which is exceptional in most of these genera has become permanent in *Pythiopsis*, which may represent a reduced *Saprolegnia*, that, finding its first swarming period sufficient, has dispensed with the more primitive second one.

Pringsheim states ('60) that the zoöspores of *Leptomitus lacteus* germinate after a single period of activity. I have seen, however, in pure cultures of this form, abundant empty membranes with every appearance of having been cast off by a diplanetic zoöspore (Fig. 118); but unfortunately, I have not observed the actual escape of the spores from them.

After its final encystment the spore may germinate at once, if conditions are favorable; or may remain for a short time capable of germination. In germination the wall of the encysted spore grows out at one or more points into as many slender tubes (Fig. 11, *a–i*), which may reach a length equal to several times the diameter of the spore without nourishment. They soon exhaust the nourishment contained in the spore, and, if more be not supplied, cease growing and die. If, on the other hand, food is accessible, growth becomes more rapid and the tubes develop into vigorous hyphæ. At the very beginning of germination, the nearly spherical nucleus of the spore takes a more elongate form and divides into two (Fig. 13); and by the repeated bipartition of these nuclei and their descendants arise all the nuclei of the hyphæ derived from the spore.

Some observations on the rate of growth of a germ tube of *Aphanomyces* sp. may be worth recording here. The tube was produced by a spore which remained encysted in the head after all the rest had passed into the second swarming stage, and was growing, therefore, without access to food (Fig. 11, *a*). At ten A.M. the tube was just visible as a slight protuberance from the spore (Fig. 11, *a*); at eleven it had reached a length of $37\mu$ (Fig. 11, *g*); and at twelve it was $52\mu$ long (Fig. 11, *i*). The effect of the absence of a supply of food is plainly shown here. While the growth during the first hour under the stimulus of the reserve materials contained in the spore amounted to $35\mu$, that of the second hour, when this supply was becoming exhausted, fell to $15\mu$.

We pass now to a comparison of the genera *Thraustotheca*, *Dictyuchus* and *Aplanes* with those already described. It has been said that the zoöspores of *Saprolegnia* and *Achlya* sometimes become encysted within the sporangium. This condition is the normal one in the genera above named, but in these the development of a mouth at the apex is wholly suppressed. In *Thraustotheca* the entire wall of the sporangium, except a narrow basal ring, breaks up after the encystment of the spores and leaves them free or slightly held together by an intermediate substance. After a time, they swarm in the laterally biciliate form, encyst again, and germinate. The sporangial wall of *Dictyuchus*, on the contrary, does not break down, and the encysted spores press each other so closely that they become irregularly polygonal. Finally they escape separately through circular perforations of the sporangial wall, just as the spores of *Achlya* escape from their cysts, and swarm in the usual second form. The close compression of the spores within the sporangium leads to a complete fusion of the encysting wall of each one with those of the others which it touches and with the sporangial wall. This must be, at least, the morphological explanation of the structure, although the membrane separating two spores may probably arise as a single one. After the escape of the spores, as above described, there is left in the sporangium a network of the apparently single walls which separated them (Fig. 112). Their escape, like that of an *Achlya* or *Saprolegnia* spore from its cyst, is a slow operation. The time from the beginning to the completion of the escape of the protoplasm of a single spore may be half an hour or even more, and several hours may be occupied in the complete emptying of the sporangium. The separate spores follow no order in their escape, but several in all parts of the sporangium may be escaping together (Fig. 16).

After its emergence the roughly globular mass contracts and becomes more elliptical, while cilia appear and slowly lengthen. At length, twenty or thirty minutes after escaping, in case of the undetermined species studied (Fig. 16), only four or six minutes after in *D. monosporus*, according to Leitgeb ('69), the spore darts away.

In *Aplanes*, according to De Bary ('88), both swarming stages are suppressed, and the spores, encysted within the sporangium, produce their germ tubes, which pierce its wall and so reach the water, and perhaps fresh nourishment. But it must be observed that their loss of the power of locomotion greatly diminishes the probability of this result. This lessened value of the sporangia as organs of propagation may explain in some measure the fact that they are rarely developed in this genus.

In *Saprolegnia* and *Achlya* those spores which encyst within the sporangium may escape and swarm in the second form, or they may germinate *in situ*. It is evident that the former condition corresponds to a sporangium of *Thraustotheca* with a permanent wall, or to one of *Dictyuchus* in which the spore cysts have remained separate, while the latter is just that which is normal for *Aplanes*. Abnormal sporangia of genera whose spores are normally diplanetic may therefore be designated as "dictyosporangia," or as "aplanosporangia," according to the degree of abnormality shown. Species of *Dictyuchus* may bear aplanosporangia.

After the emptying of the first sporangium formed from a filament, which may be termed a primary sporangium, a second one is very commonly developed from the same hypha, and after it often a tertiary one, and so on for a variable number of generations. The sporangia of the second and later generations arise by one of three different modes, in a given species. In *Leptomitus,* they are formed in basipetal succession, each segment of the hypha becoming in its turn a sporangium (Figs. 115–117). In *Saprolegnia* and *Leptolegnia,* the new sporangium begins by the upward growth of the basal wall of the old one, which continues so that the new fills the cavity of the old more or less completely (Fig. 14). It may even grow out through the mouth of the latter for some distance. It is not uncommon to see several successive sporangia thus "nested" (Fig. 15). Rarely in most species of the genus, but often in *S. monilifera,* according to De Bary ('88), the renewal of sporangia by the third mode, now to be described, occurs. The genera *Pythiopsis, Achlya, Aphanomyces, Thraustotheca, Dictyuchus* and *Apodachlya* are characterized by the cymose branching of their hyphæ in the production of new sporangia. Just below the basal wall of the primary sporangium arises a lateral branch which, after a period of growth, develops a secondary sporangium at its tip. Successive repetitions of this sympodial branching on alternate sides of the apparent axis produce a scorpioid cyme, which is usually developed with more or less regularity (Fig. 10). In *Pythiopsis* there is a more pronounced tendency to the development of a one-sided or helicoid cyme (Fig. 62). Variations from perfect regularity are, however, the rule in most forms. It often happens that a branch remains short, and forms a single sporangium with a part of the axis (Fig. 10, *3*). Less often a secondary sporangium is formed below the primary one, as in *Leptomitus.* In *Aplanes* the sporangia are so sparingly developed that the formation of secondary ones has not been observed. Hartog has stated ('88) that the sporangia of *Aphanomyces* are renewed as in *Saprolegnia,* but this is certainly not true for *A. scaber,* in which cymose branching occurs (Fig. 17); and the same condition probably exists throughout the genus.

The name *resting sporangia* has been applied to sporangium-like structures which, after being cut off from their filaments, remain unchanged for a time, but which may, under suitable conditions, develop and discharge their zoöspores in the usual way. They are evidently sporangia arrested in their development, probably by external conditions. Their simplest form is that of the ordinary sporangium, but frequently they are shorter and broader, and formed in series from the hyphæ.

*Chlamydospores.* Many of the species of *Saprolegniaceæ* may produce other structures beside the sporangia, that are organs of non-sexual propagation and may be termed chlamydospores, in the sense in which Brefeld uses that term. They are usually developed in series, as swellings at the ends of the hyphæ (Fig. 18), and in their completest development are globular in form (Fig. 19), with dense protoplasm and slightly thickened walls. The connection between the members of a series becomes very slight, and they easily fall apart. They may germinate soon after their formation or after a longer time, but constitute essentially a resting state of the plant, as compared with sporangia. Their germination consists in the production of a germ tube or hypha, from which is formed a sporangium with zoöspores after a brief growth. This distinction should be emphasized, that whereas the zoöspores are formed *within* the "resting sporangia," the chlamydospores produce them in a distinct germ tube, although the interior of the chlamydospore is often included in the cavity of the sporangium (Fig. 20).

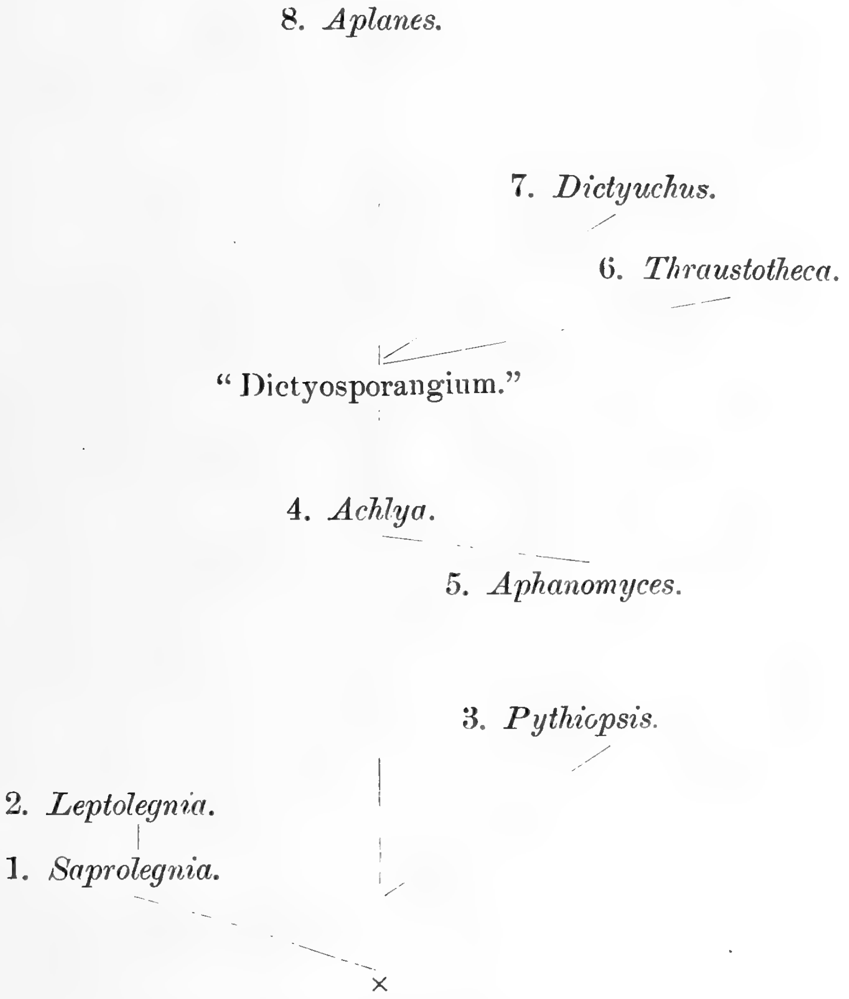
Schroeter ('69) has described the formation of "gonidia" in *Achlya*, but what he saw appear to have been rather "resting sporangia" than true chlamydospores. Walz ('70) observed and figured the latter in a species of *Saprolegnia*, and Brefeld describes ('81) similar structures. They occur also in *Aphanomyces* according to Sorokin ('76), and Zopf finds bodies of this nature to be constant and characteristic in *Apodachlya pyrifera*. But in the last case they are sometimes lateral in position, are never produced in chains, and appear to be the normal resting form of the plant. Well-developed organs of this sort have appeared in a culture of *Achlya Americana* (Fig. 18); and in one from a tank for tropical plants under glass they were abundantly produced by plants with the sporangia of *Achlya*, on which they completely replaced the usual sexual organs (Figs. 19, 20).

In comparing the organs of non-sexual reproduction in the *Saprolegniaceæ*, we observe that they do not differ in any essential feature of their origin and formation. They are, in other words, morphologically similar. But, while the office of the sporangia is the rapid propagation of the species, the chlamydospores have acquired the resting habit, and the *spore* character in the development of a germ hypha. The "resting sporangia," in their more specialized forms, constitute an evident link between normal sporangia and chlamydospores.

When considering the generic relationships within this family, and the best arrangement for indicating these relationships, one is forced to the conclusion that, notwithstanding the similarities in structure which have caused Pringsheim ('60) and Hartog ('87) to consider the differences of minor importance, yet the constriction of the hyphæ, the absence of sexual organs in most species, and their peculiarities in the single species in which they are known, with minor variations, of little weight individually, which distinguish the species of *Leptomitus* and *Apodachlya* from the others of the family, justify their separation as a distinct subfamily. The discovery of sexual organs in one of these plants, on the other hand, confirms the indication of the zoöspores that they should be included in the present family. Setting them aside, then, as *Leptomiteæ*, we may examine the genera constituting the *Saprolegnieæ*.

It is evident that the most primitive condition as regards the zoöspores is presented by the typically diplanetic form, as found in *Saprolegnia*. But the renewal of sporangia occurs most commonly, and apparently most typically, by lateral, cymose branching. Assuming as the primitive form an hypothetical one combining the two characters above indicated, we must place first in the series *Saprolegnia* and *Leptolegnia*, differing from it only in respect to the second point. *Pythiopsis* has economized by suppressing the second swarming stage, and stands alone on this line of development. In *Achlya* the first swarming has been reduced to a minimum by the mutual attraction of the spores, a newly acquired feature, and *Aphanomyces* seems best regarded as a degenerate *Achlya* rather than as a primitive one. In the remaining genera the reduction of the first swarming stage, begun in *Achlya*, is carried to complete suppression. The condition presented by a dictyosporangium of *Achlya* is in the direct line of development from the normal type of that genus, and that of the aplanosporangium is a further step on the same line. The former condition becomes modified in two ways — in *Thraustotheca*, by the early breaking up of the sporangial wall; and in *Dictyuchus*, by the coalescence of the encysting walls and the development of numerous secondary mouths instead of the original primary one. The latter condition becomes permanent and typical in *Aplanes*.

These ideas concerning the relationships of the genera may be graphically expressed as follows:



## Sexual Reproduction.

The reproductive organs of the second class are morphologically sexual, though, as will be seen later, they are not physiologically so in all cases. In the following account they will be described as sexual organs without reference to the occurrence of a definite sexual act, which will be subsequently discussed. Since they are the morphological equivalents of the truly sexual organs of related fungi, there is no occasion to change the names which they received when believed to be also their functional equivalents.

All of the described species of *Saprolegnieæ* produce sexual organs, usually after the maximum development of sporangia has been passed; indeed it is impossible to distinguish the species except by their sexual organs. None of the *Lepto-*

*miteæ* has been known heretofore to bear them, and their peculiarities in the single form in which these have been seen will be discussed in connection with the description of that species (*Apod. completa*). The special office of these organs is the production of bodies which, like the chlamydospores above described, may in some cases germinate at once, but ordinarily constitute a resting condition of the fungus. The conditions most favorable to the development of the sexual organs are not yet fully understood, and the readiness with which they are produced varies much with the species. The species of *Saprolegnia*, for instance, produce their sexual organs less freely and less certainly in cultures than do those of *Achlya*.

The sexual organs are produced, like the sporangia, from the main hyphæ or from branches, and are commonly terminal, though sometimes intercalary, in position. The female organ, the *oögonium*, develops as a swelling of the thread which bears it, which may be termed, when not a primary filament, the *oögonial branch*. The swelling increases as the protoplasm accumulates, until its definite form is reached. If the oögonium be terminal, its form is most commonly globular (Figs. 52, 71), though often with a cylindrical basal portion (Fig. 43), and sometimes ellipsoidal (Figs. 87, 99). When the extreme tip of the hypha is not involved in the swelling, it forms an apiculus to the oögonium (Figs. 27, 57). Intercalary oögonia are oftenest barrel-shaped (Fig. 59). After the form and size of the oögonium has been determined, it is separated from its hypha by a transverse wall, or, if it be intercalary, by two such walls. The formation of the walls is characterized by the same phenomena which are observed when the basal wall of the sporangium is formed. The wall of the oögonium has meanwhile been thickening by the deposit of new material upon its inner surface. In the simplest cases this deposit takes place evenly, producing a smooth wall of equal thickness throughout (Fig. 81). A somewhat less even deposit produces a roughened inner surface (Fig. 77); or the thickening may be wholly lacking on certain definite areas more or less numerously scattered over the wall of the oögonium, causing the pitting of the membrane which is a constant and characteristic feature of certain species (Figs. 43, 72). Instead of presenting a smooth outer surface, the whole membrane may be, from a very early stage, raised at intervals into outgrowths of varying height and frequency, giving it a warty or spiny appearance (Figs. 55, 104).

While the membranes of the vegetative filaments and of the sporangia always give the characteristic cellulose reaction with chloroiodide of zinc, those of the fully developed oögonia take with this reagent* a beautiful Indian-red shade, showing that

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*This was prepared by dissolving Grübler's solid chloroiodide of zinc in its own weight of water, or somewhat less, and then adding metallic iodine until the desired sherry-brown color was obtained.

some chemical change has taken place. Since the pits are marked by colorless areas in the otherwise deeply colored wall, the original membrane must have become so changed, at those points at least, that it remains uncolored by the reagent. It seems probable that the whole outer membrane assumes this character, and that the color is produced entirely in the secondary deposit.

The male organs, or *antheridia*, are, when present, almost always borne on slender lateral *antheridial branches.* In some species they are very rarely or never developed (Figs. 43, 104). Where they are present, they are not necessarily found in connection with all the oögonia (Figs. 40, 75, 76), though they may be invariably so (Figs. 52, 71, 105). The number of antheridia attached to a single oögonium shows very little tendency to definiteness, except in *A. racemosa* (Fig. 94). The most that can be said is that in a given species there is a general tendency to an abundant production of antheridia, or the reverse.

The antheridial branches arise from the main filaments or from oögonial branches, sometimes exclusively from one or the other, in other species from both. They may be very short and simple (Fig. 98), or long and much branched (Figs. 51, 71). From their tips antheridia are cut off by transverse walls, and rarely are intercalary also. The antheridia are cylindrical or clavate in form, somewhat thicker than the branches, and with slightly denser protoplasm. Their form is very constant for a given species and, in connection with their position and origin, affords important characters for specific diagnoses. Their walls show in a less marked degree the reaction of the oögonial walls.

The same primary filament may give rise to both oögonial and antheridial branches, or it may produce only those of one sort. Since it is practically impossible to determine in ordinary cultures whether two filaments belong to the same plant, and since definite cultures from a single zoöspore have not been made, we cannot say whether species whose hyphæ are unisexual are truly diœcious or not. It is safe, however, to apply to them the term used by DeBary, *diclinous* (Figs. 51, 88). The same author calls species with bisexual filaments *androgynous.* Among species of the latter kind, which constitute the large majority of the *Saprolegnieæ*, the antheridia may attach themselves to oögonia from the same or from other filaments. Most of them reach oögonia from the same hypha, probably because these are nearer.

In one species not yet met with in America, *S. hypogyna*, a single branch is bisexual, the antheridium being formed from a cell cut off by a second wall immediately below the oögonium. This is the only known case in this family of antheridia without antheridial branches.

In case of the androgynous species, the antheridial branches begin to appear soon after the oögonial ones (Fig. 21); but the antheridia have usually been formed and come into contact with the oögonium before the basal wall of the latter has appeared. Commonly they are applied by their sides to the oögonial wall, but in a few species (Figs. 54, 94) they present their ends, so that their longer axes are nearly at right angles with the wall, instead of parallel with it, as in most species.

When a certain stage in the differentiation of the contents of the oögonium has been reached, as will be described later, the antheridia give rise, in most cases, to slender tubular outgrowths from the sides applied to the oögonial wall. The tubes penetrate this wall and grow into the cavity within, remaining simple or branching. These structures are, morphologically at least, fertilization tubes. In species with pitted oögonia the antheridia are often, but not always, applied to the thin places, and the fertilization tubes can thus penetrate more easily. But the old view that the pits are perforations of the membrane for the admission of these tubes is untenable from any point of view.

The sexual organs are, then, specialized branches; but their special character does not prevent their showing occasional reversional features, recalling their primitive nature. The oögonial branch may subdivide and bear an oögonium on each division (Fig. 22). It is not uncommon to see a young oögonium which has ceased its normal development and produced one or more smaller oögonia by proliferation from its surface (Fig. 23); and I have seen in *A. Americana* a fully formed oögonium, which, after the formation of its basal wall, had reverted to the vegetative condition, so to speak, and had given rise to an oögonial and an antheridial branch which had reached their full normal development (Fig. 24). The production of an antheridial branch from the very body of an oögonium occurs so commonly as to be normal in *A. racemosa* (Fig. 96), in which the branch arises as often above the basal wall of the oögonium as below it; but the antheridium is probably cut off from its branch before the oögonium is cut off. Further proof that there is no fundamental difference between the two kinds of sexual branches may be found in the fact that antheridial branches may produce at their ends small, though abortive, oögonium-like swellings, even after giving off branchlets with normal antheridia (Fig. 25). I believe I have also seen the formation of a spore-like body in a similar swelling, as observed by Zopf ('90) in *Peronospora calotheca*, but have not been able to feel certain on this point.

Having now traced the origin of the sexual branches and the formation of the sexual organs in general, we pass to the detailed examination of the fate of their protoplasmic contents. The dense mass of protoplasm which fills the oögonium when it has attained its final form, contains, like that of the sporangium, very numerous nuclei irregularly scattered through it. The protoplasm is at first pretty evenly distributed through the cavity of the oögonium, and encloses irregular vacuoles. But it soon forms a definite parietal layer which is densest next the wall, and the vacuoles fuse into a single large central one. The nuclei are still indefinitely arranged (Fig. 30). They vary considerably in size, and in structure are identical with those of the vegetative filaments from which they are derived. After the growth of the oögonium has ceased and the protoplasm has become parietal in position, the outer walls thicken and the basal wall is formed, as already described.

After an interval the parietal protoplasm begins to undergo changes preliminary to becoming collected into one or more globular masses. We owe our first exact knowledge of these phenomena to DeBary ('81), who studied them in several species. The figures here given of the later stages of the process in a species not studied by him, *A. apiculata*, may serve at least to corroborate and supplement his account and illustrations (Figs. 26, 27). The first change observed consists in the appearance in the protoplasm of numerous light spots, approximately circular in surface view, which may be seen to slowly shift their positions and eventually to disappear. These spots were thought by Pringsheim ('58) to mark the positions of future pits in the wall, which he regarded as perforations formed by resorption. Reinke ('69), Cornu ('72), and DeBary ('81), showed that the spots are much more numerous than the pits and that they occur in all species without regard to the structure of the wall. It is undoubtedly true that they are much more numerous than the pits in pitted oögonia and that they bear no relation to them. DeBary's explanation ('81) of their nature is supported by their appearance in section (Fig. 32). They are doubtless the expression of vacuoles in the parietal protoplasmic layer, formed by accumulations of cell-sap, and finally empty into the central vacuole. Thus the central cavity becomes gradually larger and the wall-layer correspondingly thinner and denser (Fig. 33). The upper vacuole in Fig. 32 has united with the central one in Fig. 33. After the vacuoles have disappeared, the proper degree of density having been reached, as we may suppose, the protoplasm begins to flow towards certain regions and away from others, causing a heaping up at the former and a thinning at the latter places. These accumulations increase at the expense of the surrounding material until there are formed a number of pretty distinct masses connected by a thin parietal sheet of protoplasm, which is still a continuous lining of the wall (Fig. 26, *a*). This layer now breaks and its rupture is followed by a large increase in the volume of the protoplasmic masses, corresponding to the stage of swelling in the sporangium. At the same time, the basal wall, previously convex downward, becomes reversed in position, indicating a loss of turgescence, as in the sporangium; and the fragments of the parietal lining are absorbed into the masses, which we may call, following the homology of the sporangium, oösphere-origins (Fig. 26, *b*). If the rapidly shifting vacuoles present in the sporangium at this stage are also formed here, the protoplasm is too dense to permit their recognition. The oösphere origins, which, when numerous, may nearly fill the oögonium at their period of greatest swelling, now contract rather rapidly, approaching more and more nearly to the spherical form. During this process there are separated from the origins small masses of protoplasm which may move away a short distance and may remain detached for some minutes (Fig. 26, *c*); but they appear to be always taken up again by the same origins from which they were separated (Fig. 26, *d*). The rounding off is soon completed, and the oögonium contains a number of fully formed oöspheres. All the oögonia of some species, and the smallest of most others, produce only a single oösphere in each. The formation of these follows the same course as that above described for the polysporic oögonium, with certain necessary simplifications. As has been intimated, the oöspheres are normally spherical, but they may assume an ellipsoidal or cylindrical form when compelled to do so by the size and shape of the space within which they are developed.

The separation of protoplasmic fragments from the zoöspores and oöspheres during their final contraction and rounding off, and their subsequent reabsorption by their parent masses, constitute phenomena of peculiar interest. They were first observed by DeBary ('81) in connection with the oöspheres, where they are the more conspicuous; and their formation has been regarded as analogous with that of the polar bodies of the animal egg, while their reabsorption has been explained as compensating for the absence of an act of fertilization. But the fact that the nuclei of the oöspheres are reduced to one or a very few at the time of their formation makes it certain that these fragments are non-nucleate and therefore not analogous to polar bodies; while the fact of their separation from the zoöspores also removes the possibility of their sexual significance. They probably represent in their formation the persistence of some inherited phenomenon of no present functional significance, as Hartog ('92) has suggested.

It will be seen that, omitting the preliminary formation of vacuoles, the changes which characterize the formation of the oöspheres are identical with those observed in the development of the zoöspores. But the time required for the former is much longer, for the zoöspores may escape an hour after the cutting off of the sporangium, while the oöspheres may require eight hours or more for their formation.

As soon as the oöspheres are differentiated, the antheridia, when present, begin to produce the fertilization tubes, which soon reach and come into more or less close contact with the former. The tendency of the tubes to grow towards the oöspheres and to attach themselves to them is clearly marked, but does not appear to be so strong and invariably active as it has been said to be by most writers.

Each oösphere now secretes about itself a delicate cellulose wall, which gradually increases by successive deposits until it attains a considerable thickness. From the time of the appearance of the wall these bodies are no longer oöspheres, but oöspores. The fertilization tubes soon begin to fade and finally quite disappear, as do also the antheridia and even the antheridial branches, in some species.

By the earlier writers it was assumed from the fact of their presence and from the analogy of related fungi, that the tubes are functional organs of impregnation and that an actual fertilization occurs. Some, especially Pringsheim ('55, '58, '60), argued for the necessity of fertilization. This author at one time ('60) regarded certain peculiar filaments, whose peculiarity was really due to Chytridiaceous parasites, as male filaments of species which have no antheridial branches; but later ('74), he gave up this view and considered plants of the latter sort as parthenogenetic forms of sexual species. Reinke ('69) described uniciliate spermatozoid-like bodies as the fertilizing element in *S. monoica*. These were probably zoöspores of *Chytridiaceæ*. Cornu ('72) assumed and argued for the necessity of fertilization, and maintained the inability of unfertilized oöspheres to form ripe oöspores. Doubt of the existence of functional sexuality in these fungi was first expressed by DeBary ('81) and was based on his failure to observe any passage of material from tube to oösphere, or even any opening in the tube. Pringsheim ('82) opposed these views very strongly with arguments and with an account of observations of the penetration of the oöspheres by amœboid swarmers—"spermamœbæ"—developed in the fertilization tubes and set free from them. Zopf ('82) described amœboid parasites of *Saprolegniaceæ* and attributed Pringsheim's spermamœbæ to this source. Ward's observations ('83), while not extensive, confirmed DeBary's. The further discussion of the subject consisted simply in the maintenance of their former positions by those engaged, and may be followed in subsequent papers of DeBary ('83), Pringsheim ('83, '83a), Müller ('83), and Zopf ('83). The result has been that the conclusions of DeBary have generally been adopted and made the basis of discussions of the group. The writer has attempted to investigate the question independently in connection with the cytology of the sexual organs, to which we may now turn.

The structure and nuclear changes of these organs have been studied chiefly in the genera *Saprolegnia* and *Aphanomyces* by previous writers, and by the present one chiefly in *Achlya Americana* and *A. apiculata*. The method employed in these investigations has been that of serial sections. Flies well covered with hyphæ of the species to be studied, bearing abundant sexual organs in various stages of development, were fixed with a saturated aqueous solution of picric acid for twenty-four hours, in the earlier part of the work. Later, this treatment was replaced by exposure for fifteen or twenty minutes to a hot saturated aqueous solution of corrosive sublimate ($HgCl_2$). This reagent fixes the cell contents without even the slight distortion caused by picric acid, and is strongly to be recommended for such work, as has been done by Hartog ('89a). The whole specimen was, after fixation, washed and soaked in fifty per cent. alcohol, and then stained for twenty-four hours in Grenacher's or Kleinenberg's hæmatoxylin. After being washed again and passed through graded alcohols and chloroform into paraffin, in the usual manner, the fly with attached fungi was imbedded in paraffin and cut into sections about $7\mu$ in thickness by means of the Minot microtome. The sections were then mounted serially in balsam.

The very numerous nuclei carried into the young oögonium with the protoplasm exhibit the structure of the mycelial nuclei, as has been said (Fig. 30). The number of these nuclei bears no relation to the number of oöspheres to be formed, except as both are controlled by the amount of protoplasm in the oögonium. In nine sections, including the whole of a young oögonium, about $60\mu$ in diameter, of *A. apiculata*, I have counted 175 nuclear structures. With liberal allowance for the presence of parts of the same nucleus in two sections, it is not probable that the oögonium contained less than 100 nuclei; yet this species rarely produces more than five oöspheres in an oögonium. The nuclei remain passive during the formation of the central vacuole, and finally lie distributed through the parietal layer (Fig. 30). I have never been able to see any evidence of division in oögonial nuclei, and believe, with Hartog ('92) and Dangeard ('90), that it does not occur. After the formation of the parietal layer, the nuclei appear to migrate towards each other and to fuse in pairs (Fig. 31); and a little later they are seen to be much less numerous and larger, as well as far less deeply stained by hæmatoxylin (Fig. 32, 33). Indeed, a careful search with well-managed illumination is necessary for their detection. This is due to the fact that their chromatin masses largely lose their characteristic power and are masked by the granular protoplasm, while the nuclear membrane becomes barely recognizable. The space between the membrane and the chromosome, occupied by the hyaline part of the nucleus, is proportionally larger than in the vegetative nuclei; and it is probably this fact, combined with the faintness of the other parts, that has led Hartog ('89) to attribute to these fusion-nuclei the vacuolated appearance of the young oögonium. That the two conditions are quite distinct, though occurring simultaneously, as Dangeard ('90) has maintained, may be seen in Fig. 32. The observed reduction in the number of the nuclei is plainly due to nuclear fusions (Fig.

31), probably many times repeated, but whether all the original nuclei are involved in these fusions, or whether some of them degenerate and disappear like those of the periplasm of *Peronospora*, as described by Wager ('89), is uncertain. When the protoplasmic layer reaches its greatest density and regularity of arrangement, the nuclei are in this indistinct condition (Fig. 33). Just when and how they regain the vegetative structure, I am not yet able to say, having unfortunately failed to obtain sections of oögonia at the stage of the formation of the oösphere origins and of the rounding off of the oöspheres. It is certain, however, that, as Hartog has said ('89), and contrary to the statements of Dangeard ('90), the young oöspores contain but a single rather large nucleus (Fig. 35). This is commonly true also of the fully formed oöspheres, but sometimes these contain two nuclei which have not yet fused, though usually lying near together (Fig. 36). Hartog ('92) states that in *Saprolegnia* the reduction of the number of nuclei to that of the future oöspheres is completed as early as the beginning of the formation of the origins, while in *Achlya* it may be delayed until the young oöspore. My observations agree with these so far as *A. Americana* is concerned, but I have not examined any species of *Saprolegnia*. The single nucleus, or the two which are to form it, shows the structure and reactions of the vegetative nuclei.

Although its protoplasm is little denser than that of the vegetative threads, the antheridium is plurinucleate (Fig. 34, *a*). When the fertilization tube is formed, most of the protoplasm and usually all of the nuclei of the antheridium pass into it (Fig. 34, *a*). Hartog states ('92) that the nuclei of the tubes are derived by division from those of the antheridia; but, so far as *A. Americana* is concerned, I have seen no reason for supposing that nuclear divisions occur here more than in the other reproductive organs. The number of nuclei in different antheridia of this species does not vary widely, and the number in a tube corresponds pretty closely, as a rule, to the number in an antheridium (Fig. 34, *a*); and as the growth of the fertilization tube is accomplished apparently by the migration of the protoplasmic contents of the antheridium, and not by any increase in its amount, there is no *a priori* reason for nuclear division, under the circumstances. After passing into the tubes, the nuclei undergo no change. It is occasionally possible to find a fortunate section through the sexual organs and oöspores, like that figured in Fig. 34, *a*, which shows well their relations and the fate of the tubes. And one always finds that, in whatever stage of development the oöspores may be, the tubes are completely closed, as was stated by DeBary ('81), and show their walls sharply defined throughout; and that their protoplasm and nuclei are in essentially the same condition until they begin to degenerate after the complete ripening of the spores. One sometimes observes a nucleus in the very end of the tube after the wall of the oöspore has become thick and dense (Fig. 34, *a*). Since it is impossible to accept any view of fertilization which does not involve the passage of a nucleus from the tube, these facts must remove all possible doubt of the correctness of the belief expressed by DeBary that these fungi are no longer truly sexual, in spite of their fully developed sexual organs.

After the thickening of its wall, a period of a few days is necessary for the complete ripening of the oöspore. The visible sign of this process lies in the separation of the fatty material, which has been until now scattered in small globules through the protoplasm, into one or a few large and more or less spherical masses. While in certain species it characteristically remains in several portions (Fig. 68), it is commonly fused into a single drop (Fig. 111). This generally continues surrounded by protoplasm and nearly central (Figs. 95, 111), although it may be so much displaced as to leave only a thin film of protoplasm over one side. Oöspores of this type are called centric, to distinguish them from those of excentric structure, in which the oil globule or globules and the protoplasmic mass occupy opposite sides of the spore, and are in contact only by their margins (Figs. 68, 73).

After a period of rest which varies greatly in different species, the oöspores may germinate. Preparation for this process consists in the breaking up of the oil globule and its rediffusion through the protoplasm. The inner membrane of the spore now grows out through a rupture in the outer one into a short thread similar in structure to a vegetative hypha (Fig. 29, *a*). If this thread comes at once into contact with available nourishment, it may develop rhizoids and branch, and so grow directly into a new plant. But if nourishment be not immediately at hand, the hypha, after a brief growth, forms a sporangium at its apex in the manner typical of its genus. There can be no doubt that the numerous nuclei of the germ-hypha arise from the division of the single nucleus of the oöspore, but how early the division begins is not certain. Dangeard ('90) maintains that the oöspores are always multinucleate, and it may be that this division begins, at least in some species, quite early, and that therefore he has overlooked the uninucleate stage. He suggests that a difference may be found between oöspores which germinate at once and those which require a considerable period of rest. But there is no doubt that the oöspores of *A. apiculata*, which, according to DeBary ('84), germinate as soon as they are ripe, are distinctly uninucleate.

In comparing the chlamydospores and the oögonia of the *Saprolegniaceæ*, we may assume what is probably true, that no nuclear changes occur within the former. If so, then the only real differences between these two organs are found in the concentration of the protoplasmic contents of the latter into one or several separate masses and the fusion of the nuclei of these masses into one, to be restored by subsequent division. These differences are of purely physiological and sexual significance and are inheritances from the truly sexual ancestors of these plants. But on the other hand, it is evident that sporangia, chlamydospores, and oögonia are strictly homologous organs.

It is easy to speculate upon the relationships of the present family to various other groups of *Algæ* and *Phycomycetes;* but this would be of little profit. Until our knowledge of some details of the development of the plants concerned, especially of their cytology, is more complete, it seems well to refrain from further conjecture.

## OCCURRENCE AND DISTRIBUTION.

The *Saprolegniaceæ* are found more or less commonly in all fresh waters, but prefer such as are pure and clear. They occur most abundantly and develop most luxuriantly in such waters as contain and favor the growth of the pure-water Algæ, *Conjugatæ* and *Chlorophyceæ.* In stagnant waters or those which are polluted by organic matter, they may be found, but their development is usually slow and feeble, and is often quite arrested by the swarms of Bacteria and Infusoria which find their congenial conditions in such places. The most striking exception to this general statement is afforded by *Leptomitus lacteus*, which grows especially in waters containing considerable organic impurity; and the same is perhaps true of the other *Leptomiteæ.*

These plants are usually saprophytic and grow upon animal and vegetable remains. The latter may include dead, woody or herbaceous parts of vascular plants or even decaying Algæ. On the last I have found *L. lacteus* growing vigorously. But it is on animal remains that they flourish best; and of these the most favorable appear to be insect bodies. The reason for this fact probably lies in the circumstance that these bodies, being protected by a chitinous skeleton, are not so exposed to the attacks of putrefactive Bacteria, and therefore decompose slowly and cause little pollution of the surrounding water, as compared with a bit of naked flesh of the same bulk. The *Saprolegniaceæ*, too, undoubtedly act as scavengers in appropriating for their own growth the more readily available organic compounds of the dead body. In cultures in a small volume of water, the evidences of decay disappear after a few days, coincidently with, or even before the cessation of active growth in the fungus, consequent upon the exhaustion of available nourishment.

One or more species of the group are facultative parasites which can attack living fishes and Amphibia, and cause serious disease which usually results in death. Under certain conditions which are not yet well determined, the disease may become epizoötic and cause great mortality in a lake or stream or in some restricted part of it. Notices of such cases occur throughout the literature from the time of Hannover ('39) and Unger ('43) to the present. The most famous outbreak, and the one best studied, was that on salmon and some related fishes in the rivers Esk, Eden, Nith, and others in England and Scotland. The details concerning this attack and concerning the pathology of the disease may be found in the papers of Smith ('78), Stirling ('78, '79, '79 a), Brook ('79), Buckland ('80), and Huxley ('82). It is sufficient to say here that Huxley was convinced that the disease was caused by a truly parasitic *Saprolegnia*, called by all writers on the disease, *S. ferax*. The only reference to the occurrence of a similar epizoötic in America which has come to my notice, is a brief note by Gerard ('78), who reported severe mortality among fishes, from this cause, in the Passaic river in New Jersey.

Murray ('85) and Schnetzler ('87) have found that the zoöspores of "*S. ferax*" cultivated on flies can attack living fishes and frog-tadpoles and produce a growth of the fungus which kills the victim. Some facts concerning the effects of *A. racemosa* in a fish-hatchery will be discussed in connection with the description of that species.

Owing to the absence of suitable substrata for their development in mass, and the brief time required for the completion of their life-cycle, these plants are not often found growing spontaneously; and this fact has led to the belief that they are somewhat rare or difficult to obtain. But the writer's experience in the United States fully agrees with that of DeBary in Europe that this is by no means the case. The last-named author has given ('88) very practical hints for obtaining and cultivating them which it will not be superfluous to repeat here, with some additions drawn from personal experience. For reasons above stated, the most prolific source of supply is water containing green Algæ, and the best substratum is afforded by insects such as common house-flies or meal-worms. For material, a handful of Algæ may be taken from the stream, pond, or pool in which they are growing and placed in a collecting bottle or other vessel which will protect them from drying. In the laboratory, these are placed in a vessel of water from the public or private water supply, and the culture insects are thrown upon its surface. The collection of a mass of Algæ without water, except that retained by the mass, reduces the bulk of specimens, which is of importance when they are taken at a distance from the laboratory, and largely excludes aquatic organisms which might make trouble in the cultures; while experience shows that the zoöspores and oöspores of the *Saprolegniaceæ* are carried with the Algæ to a large extent. If it is desirable to avoid any possible infection from other sources than the mass of Algæ concerned, the water may be filtered, heated to boiling, and then cooled, before the specimen is placed in it. DeBary found that, in practice, the water supply of Strassburg never produced any of these fungi in cultures made with water from its pipes alone; and I have had the same experience in repeated trials with that of Amherst. But water from the Cambridge pipes, and doubtless that from others, will yield them at certain seasons, at least. The insects used may be freshly killed, and their chitinous covering should be broken as little as possible; but I have found that, for winter cultures when fresh insects are not readily available, an excellent substitute may be found in dead house-flies, collected in the fall and kept dry and exposed to the air, but protected from dust. Since the dry surfaces of insects are not readily wetted by water, it has proved useful to moisten them, whether fresh or dried, with alcohol, and then to soak them in water for a few minutes to remove the alcohol. They will then, when thrown into the culture vessel, sink until their bodies are mostly below the surface and so present a much larger area to the swimming zoöspores of *Saprolegniaceæ* than if dry and floating largely above the surface.

Since the zoöspores depend for their activity on a sufficient supply of oxygen we may expect them to be most abundant near the surface of the water, and since they are chemotactic, being strongly attracted by nutrient substances, they must readily reach the floating insects and germinate upon their bodies. An average time for the appearance of the young hyphæ is perhaps two days from the beginning of the culture, but one day is ample time, as a rule, for the zoöspores to have effected an attachment to the substratum. The insects should now be transferred to a vessel of fresh, clean water, and here the development of the fungus may be followed. The water should be carefully changed daily or less often, as may be required, until the maximum of vegetative activity is past. For superficial examination, the whole insect with attached fungi may be floated upon a slide. For more thorough study, parts seen by this preliminary method to be in the desired condition may be cut off and mounted under a cover, or used for a hanging drop culture. Rothert ('88) has pointed out that well-grown filaments with reproductive organs continue to develop normally after being cut off, until their protoplasm is exhausted.

It is not easy, although it is usually possible, to obtain from a mixed culture of several species, pure cultures of each. This may be accomplished by using sterilized water, fresh, clean insects, well-soaked in alcohol and distilled water, and a very small quantity of the fungus, preferably zoöspores from a single sporangium. A few attempts will give the desired result, if the first does not. The use of small portions of successive cultures is very useful here, as in the culture of Bacteria, in eliminating all but a given form. Many species grow well on a flooded slide in the saturated atmosphere of a moist chamber. Cultures may be pretty safely sent by mail in suitable mailing tubes for liquids, but should be sent at the proper stage of development. After some experience in this matter, it appears to the writer that the best time for mailing a specimen which will be more than a day *en route* is when the sexual organs are just fully formed. They should be placed in a tube filled with clean, preferably sterilized, water and mailed at once. If sent later, the plants are likely to fall in pieces on the way; while, if sent earlier, the close confinement for some time and the consequent vitiation of the water seem to reduce their vigor so that they subsequently fail to produce sexual organs.

The application of the above described culture methods to American materials has shown, as has been said, that these plants are not less abundant with us than in Europe. Among the many samples of material from the most varied sources, which he investigated, only one failed to furnish to DeBary some member of this family. In a large number of cultures from fresh waters of all kinds, rivers, ponds, brooks, spring-holes, drains, and rain-pools of brief duration, in short, from wherever Algæ appear, I have failed only two or three times to obtain *Saprolegniaceæ*. A single culture may often yield several species. DeBary gives seven as the largest number obtained by him from any one source. I have obtained nine species from two handfuls of moss and Algæ from a small shallow pool just at the border between a swamp and damp pine woods. On dead branches in this pool grew *Mougeotia* sp. and *Ulothricaceæ*, and over the mosses bordering it crept the filaments of a species of *Tolypothrix*. Cultures produced at once *S. diclina* and *torulosa*, *A. Americana*, *apiculata*, *racemosa*, var. *stelligera*, and *papillosa*, *Dictyuchus* sp., and *L. lacteus*. After the material had stood in an open jar near a north window for a few months, the green Algæ had disappeared, but the mosses and *Tolypothrix* had grown freely. Flies dropped into the jar soon bore *Aph. lævis* in abundance.

It is not yet possible to generalize at all concerning the distribution of the species of this family; but it seems probable that a great majority of them are likely to prove cosmopolitan. One difference has been very conspicuous, however, in the cultures I have studied; namely, that in those from the Northern States there has been a distinct predominance of species of *Achlya*, while in those from the Southern States specimens of *Saprolegnia*, if not different species, have been far more abundant.

The following synopsis of American species can, of course, be only a fragmentary representation of our flora, since it covers but few localities and these only in a desultory way. But the fact that of the thirty-four established European species, sixteen are here included, while five species previously unknown are described, shows what we may expect as the result of thorough exploration of many localities. It is hoped that the present contribution may serve to stimulate such exploration.

## Historical.

The first references to any of the *Saprolegniaceæ* appear to have been those of Ledermüller in 1760, of Wrisberg in 1765, and of Spallanzani in 1777. By these and later writers for a long time they were regarded as Algæ and were described by most under the generic name *Conferva*, which included, in its Linnæan application, the filamentous aquatic plants, generally. The earliest binomials appear to be those of the Flora Danica (1780), *Byssus aquatica*, and of Schrank (1789), *Conferva piscium.* Previous writers had seen these fungi on flies in water, but in Schrank's name is the first record of their occurrence on fishes. The earliest figures are those of the Flora Danica (1780), of Dillwyn ('09), and of Lyngbye ('19). As the early observers saw and figured only the sporangia, it is impossible to refer their plants to the proper species. It can only be said that the names *Byssus aquatica* Fl. Dan. and *Vaucheria aquatica* Lyngb. refer to species of *Achlya.* Dillwyn figured the *Conferva lactea* of Roth (1789), which is recognizable as our *Leptomitus lacteus* Ag. Gruithuisen described ('21) a fungus on the remains of a dead snail, and for the first time figured the escaping zoöspores of *Saprolegnia*, though without cilia. This form he called *Conferva ferax*, a name which was subsequently used promiscuously by many authors for any of the larger species of this family. It was first applied to a distinctly characterized form by Thuret ('50), though without an understanding of the real specific differences among these plants. Carus next ('23) described a fungus on salamander larvæ, with spores collecting in a globe at the mouth of the sporangium, which he called *Hydronema.* He observed several characteristic features in the development of the form, and recognized its points of difference from Gruithuisen's fungus. In an appendix to Carus' paper, Nees von Esenbeck ('23) established the genera *Saprolegnia* and *Achlya* on the distinctive differences in the escape of the zoöspores which we recognize as their most salient characters, to-day. He called Gruithuisen's fungus *S. molluscorum*, and Carus' form *A. prolifera;* but he apparently did not know the sexual organs, and it is impossible to identify the species intended by him. A year later, Agardh ('24) included in his genus *Leptomitus* all described *Saprolegniaceæ* under the names *L. clavatus*, *prolifer*, and *ferax*, grouping the forms of earlier writers rather according to substrata than by structure, and mixing his synonymy confusedly. Berkeley ('33) followed Agardh's generic arrangement, and called the form he figured *Leptomitus piscidicola.*

After brief and unimportant mention of these plants in earlier papers, Meyen described ('39) some features of the development and escape of the spores and of their germination. He also observed dictyosporangia. Now followed a series of accounts of observations concerning the attacks of *Saprolegniaceæ* on aquatic Vertebrates by Hannover ('39 and '42), Stilling ('41), Bennett ('41), and Goodsir ('42). These papers contained little of real importance except Hannover's second one, which has been before mentioned as containing the first good account of the development and later history of the zoöspores. Unger's account ('43) was in some respects less complete than that of Hannover. All the writers yet mentioned dealt only with the sporangia, in most cases of the *Saprolegnia* type; but nearly all called their plants *Achlya prolifera.* In Schleiden's "Grundzüge" ('45), we find the first account of a second and larger sort of spores, which we now know as the oöspores. These were again mentioned by Naegeli ('47) and by Braun ('51), the latter of whom also described the antheridial branches. Naegeli ('47) speaks of a third sort of reproductive organs, which were probably, like those described by Cienkowski ('55) the sporangia of parasitic *Chytridiaceæ* of the genus *Olpidiopsis.* The general features of the development of both sporangia and oögonia were described at this time by Thuret ('50), who then first demonstrated the biciliate character of the zoöspores of *Saprolegnia*, and figured unmistakably the oögonia of the form he studied, which he called *S. ferax.* Now followed those accounts by Pringsheim ('51) and DeBary ('52), which mark the beginning of our exact knowledge of the *Saprolegniaceæ*, and which have led to the long series of contributions, the most important of which are quoted in the morphological and systematic parts of the present paper. The number of these which we owe neither to the researches nor to the direct influence of these two pioneers and masters in the study of the Thallophytes is surprisingly small.

To return to the systematic history of the group: Kützing, in his "Phycologia" ('43), places *L. lacteus*, with various other forms not *Saprolegniaceæ* and largely unidentifiable, under the genus *Leptomitus*, and includes the other forms then known under three species of *Saprolegnia*, *S. minor*, *ferax*, and *xylophila.* In his "Species Algarum" ('49) the same author includes *L. lacteus* as before, and enumerates six additional species of *Saprolegnia*, most of which are now unrecognizable. Braun ('50) established the species *S. capitulifera* for a plant with sporangia of the *Achlya* type. Robin ('53) mentions only *S. minor* and *S. ferax;* and Pringsheim, in his earliest paper ('51), though describing a *Saprolegnia*, calls it *A. prolifera.* It was DeBary ('52) who first again brought forward and applied Nees' old generic distinctions, and showed the necessity for characters drawn from the sexual organs in specific determinations. It is to him and to subsequent writers who recognized the correctness of his position, that we owe our present notions of generic and specific distinctions. No writer before him appreciated the true specific differences, and none save Nees, whose insight remained unrecognized for three decades, saw the true value of characters now recognized as generic. With the single exception of Thuret's *S. ferax*, no species had previously been described or figured so as to be now recognizable. It is an interesting coincidence that his first botanical publication and the posthumous fragment prepared from his last manuscripts by his successor should both have dealt with *Saprolegniaceæ.*

The history of the great progress in the knowledge of this family during the past forty years may be traced, as has been said, in the works referred to on other pages; but certain matters which are now wholly of historical interest may be briefly referred to here. The discussions concerning the specific value of certain morphological differences and concerning the sexuality of these fungi are considered sufficiently elsewhere. But the members of this family have figured prominently in the pleomorphy craze which followed Tulasne's proof of the pleomorphism of many *Ascomycetes.* The extreme advocates of this doctrine, Bail ('60), Hoffman ('67), and Karsten ('69), held that the same plant assumes the form of *Saprolegnia* in water, or of *Empusa* in air, when growing on flies. On other substances the same species was supposed to appear as *Mucor*, or even as *Penicillium;* and in saccharine solutions to take the *Saccharomyces* form. Earlier than these views became popular, similar suggestions had been made. Nees ('31) suggested a connection between *Empusa* and *Achlya;* and Meyen and Cienkowski ('55) affirmed a connection between *Isaria* or *Empusa*, on one hand, with "*Achlya prolifera*," on the other. It is to Brefeld's researches ('71) and the application of rigid culture methods like his that we owe the final proof of the incorrectness of this belief.

The history of American studies of *Saprolegniaceæ* is briefly told. So far as I know, Leidy ('50) first mentioned "*Achlya prolifera*," which he reported having seen in all stages of development on Ascarids in water. Gerard's ('78) brief account of "*S. ferax*" in connection with an epizoötic among fish in New Jersey, Hine's ('78) observations on a species of *Saprolegnia* and on *Achlya racemosa*, and Galloway's ('91) cytological notes on *S. monoica* complete the short list.

## SYSTEMATIC PART.

The following diagnoses of American species of *Saprolegniaceæ* are drawn wholly from American specimens, except in a very few cases where the incompleteness of the material has made it necessary to refer to European descriptions for certain details. In all such cases the borrowed matter has been indicated by quotation marks. For species not yet known to be American a brief informal statement of the chief diagnostic characters is given to aid the student who may meet with them, since many of them are likely to be found with us.

Artificial dichotomous keys to all the intelligibly described species are prefixed to the detailed accounts, in all but the smallest genera, as a practical encouragement to their study; but they should never be relied on alone for the determination of species.

## SAPROLEGNIACEÆ Pringsh. ('57).

Aquatic fungi, living as saprophytes or facultative parasites, with usually branched mycelium; the hyphæ in a few species constricted at intervals, but remaining unseptate except in the formation of reproductive organs. The latter of two kinds, non-sexual and sexual, both formed from the hyphæ and separated from their vegetative portions by transverse walls. Non-sexual propagation by means of biciliate, often diplanetic, zoöspores, produced in cylindrical or swollen sporangia; or very rarely by homologous non-motile bodies; occasionally also by chlamydospores. Morphologically sexual reproduction by oöspores developed in typically globular oögonia, one or more from the entire protoplasm of each oögonium; antheridia on branches of androgynous or diclinous origin, very rarely on the oögonial branch, uniting with all, or with only a part of the oögonia, or in several species wholly absent; when present, usually producing fertilization tubes which remain closed, at least in some species.

### *Key to Genera.*

| | | |
|---|---|---|
| *A.* | Vegetative filaments with their walls unconstricted | (*Saprolegnieæ*) *B.* |
| | Vegetative filaments deeply constricted at intervals | (*Leptomiteæ*) *I.* |
| *B.* | Zoöspores normally leaving the sporangium by a common mouth | *C.* |
| | Zoöspores not leaving the sporangium by a common mouth | *G.* |
| *C.* | Zoöspores swarming separately on escaping from the sporangium | *D.* |
| | Zoöspores collecting in a hollow sphere at the mouth, on escaping | *F.* |
| *D.* | Zoöspores diplanetic; new sporangia growing through the empty ones | *E.* |
| | Zoöspores monoplanetic; sporangia renewed by cymose branching | PYTHIOPSIS. |
| *E.* | Oöspore single, wholly filling the oögonium | *Leptolegnia.* |
| | Oöspores one or more, not wholly filling the oögonium | SAPROLEGNIA. |
| *F.* | Sporangia usually broader than the vegetative hyphæ; zoöspores irregularly arranged | ACHLYA. |
| | Sporangia equaling the vegetative hyphæ in breadth; zoöspores in a single file | APHANOMYCES. |
| *G.* | Zoöspores encysting within the sporangium, afterwards swarming | *H.* |
| | Zoöspores encysting and germinating within the sporangium, never swarming | *Aplanes* |
| *H.* | Zoöspores set free by the breaking up of the sporangial wall | *Thraustotheca.* |
| | Zoöspores escaping each by a separate perforation of the sporangial wall, leaving a "net." | DICTYUCHUS. |
| *I.* | Zoöspores swarming separately on escaping | LEPTOMITUS. |
| | Zoöspores collecting at the mouth of the sporangium, on escaping | APODACHLYA. |

### *Subfamily Saprolegnieæ.*

### **Saprolegnia** Nees ab Esenb. ('23).

Syn. : ? *Conferva piscium* Schrank (1789).
*Conferva ferax* Gruith. ('21).
*S. molluscorum* Nees ab Esenb. ('23).
*Leptomitus clavatus* Ag. ('24).
" *ferax* Ag. ('24).
" *piscidicola* Berk. ('33).
*Achlya prolifera* Auct.
Exsic. : Myc. Univ., 1213 (*S. ferax*).
Algues de la France, 1195 (*do.*).

Hyphæ rather stout or slender, often not much branched. Zoösporangia formed from their tips, generally cylindrical or slightly clavate, rarely short and in series; the later ones arising within the empty membranes of preceding ones by upward growth of their basal walls, or rarely beside them by cymose branching. Zoöspores diplanetic, at first pyriform, with two apical cilia, escaping by a usually terminal mouth at the apex of a distinct papilla, and swarming separately; after encystment and rest becoming reniform swarmers with two lateral cilia; finally encysting again and germinating. Oögonia terminal or intercalary, never wholly filled by the one or more oöspores. Antheridia wholly absent in some species, and always present in some.

### *Key to recognized Species.*

| | | |
|---|---|---|
| *a.* | Oögonial wall always smooth and unpitted; oöspores excentric | *S. anisospora.* |
| | Oögonial wall pitted, at least in some specimens; oöspores centric | *b.* |
| | Oögonial wall spiny; oöspores centric | *i.* |
| *b.* | Oögonia in moniliform series, early falling apart, not all pitted | *S. monilifera.* |
| | Oögonia not separating from the plants before maturity, all more or less pitted | *c.* |
| *c.* | Antheridial branches attached to every oögonium | *d.* |
| | Antheridial branches attached to some or to none of the oögonia | *f.* |
| *d.* | Plants diclinous; pits small | S. DICLINA. |
| | Plants androgynous; pits large | *e.* |
| *e.* | Oögonial branch short and straight | S. MONOICA. |
| | Oögonial branch usually helically coiled | *S. spiralis.* |
| *f.* | Antheridial branches often developed | S. MIXTA. |
| | Antheridial branches very rarely or never developed | *g.* |
| *g.* | Antheridium formed just below the oögonium, on the same branch | *S. hypogyna.* |
| | Antheridia not developed, or very rarely so | *h.* |
| *h.* | Oögonia irregular, often in torulose series, with few and small pits | S. TORULOSA. |
| | Oögonia globular, or not rarely cylindrical, not in series, with large pits | S. FERAX. |
| *i.* | Oöspores one or two in an oögonium; hyphæ slender | S. ASTEROPHORA. |
| | Oöspores several in an oögonium; hyphæ very stout | S. TRELEASEANA. |

### SAPROLEGNIA MONOICA Pringsh. ('57).

Syn. : *S. ferax* Auct. *p. p.*
*S. dioica* Pringsh. ('60).
*Diplanes saprolegnioides* Leitgeb. ('68).
*Achlya intermedia* Bail ('60a), sec. Lindstedt ('72).

Ill. : Pringsheim, '57, Pl. XIX, XX.
Reinke, '69, Pl. XII.
DeBary, '81, Pl. V, Figs. 11–19; VI, 1, 2.
Ward, '83, Pl. XXII, Figs. 17–22.
Rothert, '88, Pl. X, Figs. 14.
*Pl. XVI, Figs. 37–39.*

Hyphæ rather stout, often long. Zoösporangia cylindric-clavate. Oögonia terminal or rarely intercalary, usually on short lateral branches, globular, their walls abundantly and prominently marked with large pits. Antheridia long-cylindrical, uniting with every oögonium, on rather stout branches of androgynous origin, which usually arise from the main hypha near the oögonial branch. Oöspores commonly not above ten, rarely numerous, centric, their average diameter about 26$\mu$.

Massachusetts—Cambridge, *Trelease;* Amherst: Alabama—Auburn, *Atkinson.* Europe.

This species, obtained by Prof. Trelease at Cambridge in 1881, was first procured by the writer from a pool containing dead *Carex* leaves, which bore abundant masses of *Chætophora;* and subsequently from a mass of dead leaves and slime at the bottom of a ditch draining cultivated fields. Among cultures from the Southern States, it has appeared only once. It does not, therefore, seem to be very abundant with us; but it is well distinguished by the large and numerous oögonial pits and the abundant and well-developed antheridia, which are larger and more conspicuous than those of any other species of the genus, except possibly *S. asterophora.*

The observation of the diplanetism of the zoöspores of this species led Leitgeb to establish a new genus, *Diplanes,* for it, although the phenomenon had previously been observed in species of this genus. Lindstedt gives *Achlya intermedia* Bail as a synonym of *Diplanes saprolegnioides* Leitg., and is followed by Saccardo ('88). Having been unable to examine Bail's description and figure, I must be content with following the authors mentioned.

#### Var. *montana* DeBary ('88.)

Differs from the type in its slightly or not at all pitted oögonia, on longer branches. It has not been recognized in America.

### *Saprolegnia spiralis* Cornu ('72.)

This form, which appears to have been recognized only by its author, is said to differ from *S. monoica* chiefly in its longer oögonial branches, which are coiled in a helix of one or two turns. It is of doubtful autonomy, but, in the absence of fuller knowledge, may be allowed to stand for the present; although it would hardly appear to be entitled to more than varietal rank, if well marked.

### SAPROLEGNIA MIXTA DeBary ('83).

Syn.: *S. ferax* Auct. *p. p.*
*S. ferax* Schroeter ('86).
*S. dioica* Schroeter ('69).

Ill.: *Pl. XVI, Figs. 40–42.*

Hyphæ rather slender, not long. Zoösporangia cylindric-clavate. Oögonia terminal or rarely intercalary, on main filaments or lateral branches, globular, with numerous pits of varying size, but often pretty large. Antheridia cylindrical, rather shorter and smaller than in *S. monoica*, of androgynous or diclinous origin, absent from a part of the oögonia, sometimes from a large part. Oöspores up to fifteen or occasionally more than twice that number, centric, their average diameter about 26$\mu$.

Pennsylvania—Philadelphia, *Keller:* Mississippi—Starkville, *White:* Louisiana —Bayou Tortue, *Langlois.* Europe.

I have not yet with certainty recognized this species in Amherst cultures, but have received it from three sources; which indicates that it is widely distributed and not uncommon. The materials for two of the cultures containing it were taken from small pools, while the third and most abundant specimen came from Algæ and *Lemnæ* growing in Bayou Tortue, near St. Martinville, La.

The species is rather vague and unsatisfactorily defined, as DeBary has remarked ('88). It is intermediate in several respects between *S. monoica* and *S. ferax*, and might seem to afford ground for regarding all these as forms of a single species, as Pringsheim does. Having found *S. monoica* and *S. ferax* to be well marked and constant before meeting with this species, I was for some time skeptical concerning it, thinking it might have originated in a mixture of those two. But the receipt of material from distinct sources which could be referred to neither of those, and which shows constantly the characters above stated, in successive generations, has convinced me that the species is well founded and appropriately named. The smaller and less abundant antheridia, not always of androgynous origin, and the usually less numerous and less conspicuous pits of the oögonial wall chiefly distinguish it from *S. monoica.* Its hyphæ are also rather slenderer and more flaccid than those of the latter.

The description of *S. ferax* given by Schroeter ('86) is clearly not applicable to that species, but very well characterizes the present one. It must be considered, therefore, that this author's *S. ferax* belongs here as a synonym; and, if so, then also his *S. dioica*, which he quotes ('86) as a synonym of his *S. ferax.* Fortunately, the name *S. dioica* had been used for another plant by Pringsheim ('60) and therefore cannot be retained for this one, although Schroeter's use of it antedates DeBary's.

### SAPROLEGNIA FERAX (Gruith.) Thuret ('50).

Syn. : *S. ferax* Auct. *p.p.*
*Achlya prolifera* Pringsh. ('51).
*S. Thureti* DeBary ('81).

Ill. : Thuret, '50, Pl. XVI.
Pringsheim, '51, Pl. XLVI–L.
Pringsheim, '74, Pl. XVIII, Figs. 5 and 11.
DeBary, '81, Pl. V, Figs. 1–10.
Rothert, '88, Pl. X, Figs. 1–13.
*Pl. XVI, Figs. 43–45.*

Hyphæ of medium size. Zoösporangia clavate-cylindrical. Oögonia terminal or sometimes intercalary on main hyphæ or lateral branches, globular or not rarely cylindrical, their walls very thickly and conspicuously marked by large pits. Antheridial branches and antheridia never developed or extremely rare. Oöspores up to twenty in an oögonium, or sometimes more ("40 to over 50," DeBary), centric, their average diameter about 26$\mu$.

Massachusetts—Amherst: Wisconsin—Madison, *Trelease:* Missouri—St. Louis, *Trelease:* Kentucky—Lexington, comm. *Keller.* Europe.

In Wisconsin this species was obtained by Prof. Trelease from Algæ collected in a ditch, and at St. Louis it grew spontaneously on flies in water. The Kentucky specimen sent by Dr. Keller was obtained from Algæ, chiefly *Hydrodictyon*, collected in a pool in a cemetery at Lexington. I have never obtained it in Amherst from open-air materials, but have found it on flies thrown in water taken from the room for tropical aquatics in the plant house of the Massachusetts Agricultural College. This specimen was a reduced form in all respects, although undoubtedly of this species.

This plant seems, then, to be more common in the Western than in the Eastern States. The absence of antheridia, the rather common occurrence of cylindrical oögonia, and the very conspicuous pitting of all the oögonia mark the species unmistakably. It was first sharply distinguished and characterized by DeBary ('81), who called it *S. Thureti*, recognizing it as the form whose oögonia were first figured by Thuret. But although, as has been remarked, the latter author had no understanding of the true specific limits among these fungi, there is still no reason for refusing to restrict to his form Gruithuisen's name, by which he called it, and which had previously been used in a much wider application.

It has already been pointed out that the *S. ferax* (Gruith.) of Schroeter ('86) is probably *S. mixta* DeBary. The description given in Saccardo's Sylloge ('88) under the name of *S. ferax* is quite unrecognizable. It is noteworthy that this work perpetuates the old myth that *Empusa* is an imperfect state of *S. ferax.*

It is difficult to circumscribe what DeBary has called the *ferax* group of *Saprolegniæ*, since so many species show relations with each other at various points, while remaining, within their limits, very constant. The three species already described constitute, however, the most closely united group, and it is perhaps better to limit the term to them, if it is to be used at all, than to apply it to an assemblage of species necessarily much larger if at all increased. In these species, taken in the order in which they are here placed, there is observed a progressive reduction in the antheridia, and an increase in the normal size of the oögonia and in the number of oöspores; while the average size of the latter varies little, although extreme specimens may vary as much as 5$\mu$ on either side of the average.

### *Saprolegnia hypogyna* Pringsh. ('74).

Syn.: *S. ferax,* var. *hypogyna* Pringsh. ('74). Ill.: Pringsheim, '74, Pl. XVIII, Figs. 9, 10.

This species, which has been studied by Pringsheim and DeBary ('88) and is doubtless well founded, differs from all other known *Saprolegniaceæ* in producing antheridia without special antheridial branches. A second portion of the oögonial branch is cut off just below the oögonium and constitutes the antheridium. Its upper wall, which is also the basal wall of the oögonium, grows up, as a fertilization tube, into the cavity of the latter. The oögonia show, in their form, in the pitting of their walls, and in the structure and number of their oöspores, near relations with the *ferax* group, but the species is at once recognizable by the peculiarities above mentioned. It is not yet known to occur in America.

### SAPROLEGNIA TORULOSA DeBary ('81).

Ill.: DeBary, '81, Pl. VI, Figs. 3–17.
*Pl. XVI, Figs. 46–49.*

Hyphæ rather slender. Zoösporangia from cylindric becoming clavate, fusiform, or nearly globular, often in torulose series. Oögonia globular, ovate, pyriform, or cylindrical, terminal or intercalary, commonly in torulose series, their walls more or less abundantly marked by small pits, and yellowish brown when old. The members of a series may form, some sporangia and others oögonia. Antheridia very rarely present. Oöspores as many as twelve, or rarely more, in an oögonium, centric, their average diameter about 25μ.

Massachusetts—Amherst: New Hampshire—Mt. Washington, *Thaxter*: Louisiana—St. Martinville, *Langlois*. Europe.

A characteristic species which is not very uncommon with us, apparently. In my Amherst cultures it has appeared twice, once from the very prolific mossy pool, mentioned elsewhere, and again from algæ (*Spirogyra*) from a small boggy area by a brook. Prof. Thaxter has sent me specimens developed spontaneously on Lepidopterous larvæ in the "Alpine Garden," on Mount Washington; and Mr. Langlois has obtained it from a ditch in Louisiana. It shows some points of affinity with the *ferax* group, as here limited, yet is very distinct. The antheridia have not disappeared quite so completely as in *S. ferax;* and the oögonia contain less numerous oöspores, while their walls are much less pitted and are more deeply colored when mature than in any of the previous species. American specimens do not quite meet DeBary's character, "mit wenigen oder ganz ohne Tüpfel," as they always have, so far as my observation of a large number of individuals goes, some pits, and often a considerable number; but these are always small.

The best diagnostic character of the species is found in the successive formation of walls in the same filament, cutting off as many segments, which may all become sporangia, or all oögonia, or partly each. In the latter case, the terminal members usually become oögonia. The oögonia remain attached to the plant until the hyphæ become disorganized, and therein differ from those of the next species. No better evidence could be desired of the lack of fundamental difference between sporangia and oögonia than the indiscriminate formation of both from exactly similar members, at the same time, here observed.

### *Saprolegnia monilifera* DeBary ('88).

Ill.: DeBary, '88, Pl. IX, Fig. 6.

DeBary separates this species as a distinct type from the other members of the genus, although, judging from his description, it would seem to represent a further development on the lines of *S. torulosa.* Its oögonia are formed in somewhat more definite moniliform chains, all of whose members appear to have the same fate.

Their walls are occasionally pitted, and no antheridia are developed. A striking feature is the separation of the oögonia from the plant and from each other, often at a very early stage, so that they lie free in the water and complete their development independently.

The species presents a transitional feature leading towards *Achlya*, or a reversional feature towards the commonest condition in the family, in that many of the later sporangia are produced by cymose branching, instead of by the usual method for *Saprolegnia*. It has not been seen in America.

### SAPROLEGNIA DICLINA nom. nov.

Syn.: *S. dioica* DeBary ('88).
nec *S. dioica* Pringsh. ('60), nec Schroet. ('69).

Ill.: DeBary, '88, Pl. X, Figs. 12, 13.
*Pl. XVII, Figs. 50–53.*

Hyphæ slender, not long. Zöosporangia nearly cylindrical. Oögonia terminal on main hyphæ, or less commonly on lateral branches, typically globular, their walls marked with small pits, which are often few and inconspicuous. Antheridial branches long, flexuous, and very slender, of diclinous origin. Antheridia on every oögonium, ovate or short clavate, often very abundant and covering much of its surface, sometimes rather few. Oöspores most commonly ten or twelve, sometimes twenty or more, and often only four to six, centric, their average diameter about 25$\mu$.

Massachusetts—Amherst: Pennsylvania—Philadelphia, *Keller:* Alabama—Auburn, *Atkinson:* Louisiana—St. Martinville, *Langlois.* Europe.

This is unquestionably our commonest *Saprolegnia.* I have obtained it six or seven times in cultures from small pools, spring-holes, and similar places, and have received it from most of my correspondents, as above shown. It is readily identified by the small and fewer pits of the oögonial wall, as compared with those of the *ferax* group; and especially by the antheridia, which are always present, as in *S. monoica*, but smaller, of different shape, and on slenderer branches than in the latter species; while the branches are always of diclinous origin. When the plants become old, these delicate antheridial branches often disappear, leaving the antheridia adhering to the oögonia without indication of their origin. This may, indeed, happen in other species, but not so commonly or so early as in the present one.

A reduced form of this species, hardly worthy of varietal rank, occurs frequently. It is distinguished chiefly by its smaller size, and by a reduction of the number of both oöspores and antheridia to a very few (Fig. 53).

The species, as limited in America, is exactly *S. dioica* DeBary, except that I have never seen the intercalary barrel-shaped oögonia, said by that author to occur sometimes. It should bear his name, but for the fact that that name had previously been applied by Pringsheim ('60) to *S. monoica* attacked by Chytridiaceous parasites; and this previous use of the name, although it can stand only as a synonym, should debar its further use, in the interest of clearness and accuracy. The use of the same name by Schroeter ('69) for apparently another species has been already alluded to. It may be, as DeBary intimates ('88), that this species has been included by some authors under the name *S. dioica;* but there is not the least evidence that the original author of that name even knew it. In order to change its name as little as possible, and yet sufficiently, I propose for the species that of *S. diclina*, which refers to the same peculiarity as did the former one.

An error which has been overlooked in reading the proof of Saccardo's Sylloge ('88, p. 269) makes what is intended for *S. dioica* read *S. divisa.* The description which follows refers to Pringsheim's pseudo-species.

### *Saprolegnia anisospora* DeBary ('88).

Ill.: DeBary, '88, Pl. IX, Fig. 4.

This European species takes its name from the fact that its sporangia are of two kinds, producing respectively large and small zoöspores. These are said to agree perfectly in structure and development, but the larger are of about twice the diameter of the smaller, which are like those of other species of *Saprolegnia.* The oögonial walls are unpitted and the antheridia agree with those of *S. diclina* in their form and in their diclinous origin. This is the only known *Saprolegnia* which has excentric oöspores. DeBary well remarks that the species deserves further study.

### SAPROLEGNIA ASTEROPHORA De Bary ('60).

Ill. : DeBary, '60, Pl. XX, Figs. 25–27.
DeBary, '81, Pl. VI, Fig. 18–29.
*Pl. XVII, Figs. 54, 55.*

Hyphæ slender, "with cylindric-clavate zoösporangia." Oögonia terminal, globular, with several or many rather long, blunt outgrowths of the wall, giving it a starlike appearance; the wall unpitted. Antheridia "usually present," on branches arising just below the oögonia from the oögonial branches, short-clavate, applied by their ends. Oöspores commonly single, sometimes two or rarely three, centric, thick-walled, their diameter about 30$\mu$.

Massachusetts—Cambridge and Wood's Holl, *Trelease.* Europe.

I have never had the opportunity of studying this species alive, and hence arises the necessity for referring to DeBary's description ('88) for some details. It occurs in preparations made by Prof. Trelease from cultures made in Eastern Massachusetts, and must therefore be included in our flora. It has hitherto been the only known member of the genus with spiny oögonia, and is readily distinguished from the second such species, next to be described, by its globular and few-spored oögonia, borne on slender threads.

## SAPROLEGNIA TRELEASEANA sp. nov.

Ill.: *Pl. XVII, Figs. 56–59.*

Hyphæ very thick. Zoösporangia cylindric, rare. Oögonia terminal or intercalary, on main hyphæ, elliptical or globular, when terminal usually ending in a strongly developed apiculus; their walls not pitted, but with rather scattered blunt outgrowths of varying length, oftenest short. Antheridial branches short and slender, arising just outside the oögonial wall, one or several to each oögonium, or sometimes wholly absent. Antheridia short-cylindric or slightly clavate. Oöspores numerous, averaging ten or twelve in an oögonium, centric, their diameter from 25 to 35$\mu$.

Massachusetts—Wood's Holl, *Trelease.*

It is a great pleasure to dedicate this very striking species to its discoverer, Prof. William Trelease, of St. Louis, whose early studies of our *Saprolegniaceæ* were unfortunately cut short by other engagements. This is done as a slight acknowledgment of the valuable additions to the present paper which are due to his generosity, and in recognition of the high character of his work as a botanist.

The species was obtained by him in 1881 in cultures with material from Wood's Holl, Mass., and he has communicated all his notes and material to the writer. It has very coarse and freely branched hyphæ which often considerably exceed 100$\mu$ in diameter at the base. The sporangia are so rare that Prof. Trelease observed only one (Fig. 56), and I have been unable to find any in his material. The size and manner of branching of the hyphæ, as well as the appearance of the oögonia, strongly suggest the genus *Achlya*, but the single sporangium seen showed that the spores escape as in *Saprolegnia.* In the structure of its sexual organs this plant resembles quite strikingly that to be described later as *Achlya papillata*, but it is much more robust than that and sufficiently distinct otherwise, aside from the differences in the sporangia.

### SPECIES INQUIRENDÆ.

*Saprolegnia androgyna* Archer ('67.) See Notes on *Aplanes.*

*Saprolegnia xylophila* Kütz. ('43). As various members of this family grow readily on decaying wood in water, it is probable that this name refers to some of them. As it antedates the discovery of the sexual organs, Kützing's figure shows only the zoösporic stage, and the name cannot be referred to the synonymy of any particular species.

*Saprolegnia corcagiensis* Hartog ('87) is said to have the constrictions and zoösporangia of *Leptomitus lacteus,* and oögonia with pitted walls ("fenestratis"). It has been recognized only by Hartog and needs to be more completely characterized and further investigated.

*Saprolegnia quisquiliarum* Roumeg. ('91) has not to my knowledge been fully described, but is based on specimens issued as No. 5932 of the "Fungi Gallici." An examination of one of the specimens issued, made partly by my friend, Mr. A. B. Seymour, and partly by myself through his kindness, failed to discover anything Saprolegniaceous.

### SPECIES EXCLUDENDÆ.

*Saprolegnia minor* Kütz. ('43) is probably an *Empusa.*

*Saprolegnia DeBaryi* Walz ('70) is probably a species of *Pythium.*

*Saprolegnia siliquæformis* Reinsch ('78) is *Monoblepharis prolifera* Cornu, according to Cornu ('77).

*Saprolegnia Schachtii* Frank ('81) is probably also a *Pythium.*

*Saprolegnia Libertiæ* (Bory) Ktz. ('49) and three other names published by Kützing at the same time, viz., *S. candida, S. tenuis* and *S. saccata,* are followed by descriptions so imperfect as to have no individuality and no value.

*Saprolegnia mucophaga* Smith (Gard. Chron., XX, 781; 1883) and

*Saprolegnia philomukes* Smith (Gard. Chron., XXII, 245; 1884) do not belong to this family. They may be forms of *Pythium.*

### *Leptolegnia* DeBary ('88).

Differs from *Saprolegnia* in that the oögonium contains a single oöspore which completely fills it.

### *Leptolegnia caudata* DeBary ('88).

Ill.: DeBary, '88, Pl. IX, Fig. 5.

The single known species of this genus has narrow sporangia, ovate oögonia on short racemose branches, and antheridia, usually one to each oögonium, on branches of diclinous origin. It was obtained by DeBary from two different cultures from German mountain lakes, and is known only from these.

## **Pythiopsis** DeBary ('88).

Hyphæ slender, much branched. Zoösporangia formed from their tips, globular, oval, ovate, or short-clavate, the later ones arising by cymose branching of the hyphæ, either sessile or on long branches. Zoöspores ovate, apically biciliate, escaping by a usually terminal mouth at the apex of a distinct papilla, and swarming separately; after encystment germinating without a second swarming stage, *i. e.*, monoplanetic. Oögonia and antheridia abundantly developed.

### PYTHIOPSIS CYMOSA DeBary ('88).

Ill.: DeBary, '88, Pl. IX, Fig. 1.
*Pl. XVII, Fig. 60-68.*

Hyphæ slender, short. Zoösporangia from globular to short-clavate. Oögonia commonly terminal and globular, their walls unpitted, sometimes with a very few blunt outgrowths. Antheridia clavate, one, or rarely more, on each oögonium, usually arising just below its basal wall, rarely of diclinous origin. Oöspores single, or very rarely two, in the oögonium, excentric, with several oil-globules, their average diameter about 18$\mu$.

Massachusetts—Amherst. Europe.

The present interesting species, previously known only from DeBary's account, and obtained by him from a snow-water pool in the Vosges mountains, appeared in two of my cultures in March, 1892. Both were obtained from Algæ consisting chiefly of *Spirogyra* sp. One, from a ditch, had been kept in a jar in the laboratory since the preceding November, and had yielded *A. apiculata*, *Aph. scaber*, and *Dic-*

*tyuchus* sp. The other was freshly collected and gave also *A. cornuta*, *A. megasperma*, and *S. torulosa*.

I have not followed the zoöspore from its encystment to its germination; but, as the spores germinate freely in cultures which contain no trace of empty membranes, such as are seen with germinating diplanetic spores, there can be no doubt of their monoplanetism. The general appearance of the plant and of its sporangia strongly suggests a *Pythium*, as intimated in the generic name. The formation of the zoöspores does not appear to follow the course above described as characteristic of the family. I have not been able to study the process in detail, but it seems to be much simpler than that usual among *Saprolegniaceæ*. While the escape-papilla may appear more than three hours before the exit of the spores, no change is evident in the protoplasm of the sporangium until fifteen or twenty minutes before that event. The separation of the spores within the sporangium is very slight and I have seen nothing corresponding to the two separation stages, with an intermediate stage of swelling up. One might regard tbis as leading towards the simpler zoöspore formation of the *Peronosporeæ*, but for the fact that the zoöspores are terminally, and not laterally, biciliate. The whole question deserves careful comparative study.

The outgrowths of the oögonial wall are only exceptionally rather long; and in the great majority of cases are not at all developed. In a very large number of oögonia examined, I have seen only one (Fig. 67) with more than a single oöspore. DeBary states that three sometimes occur. He also mentions the presence of as many as four antheridia on an oögonium. Amherst specimens have rarely had more than one each and never more than two. I have seen, also, the peculiar hyaline outer layer surrounding some oögonia, which was mentioned by DeBary; but cannot regard it as due to an extrusion of periplasm, as is suggested in his account ('88), since no periplasm is observed in other oögonia, and because it may occur on young oögonia before the formation of the oösphere, as well as on adult ones. I am, however, quite unable to explain its origin. On young oögonia it appears to be thicker than on older ones, but it has been seen at all in my cultures only exceptionally.

## **Achlya** Nees ab Esenb. ('23).

Syn.: *Byssus aquatica* Fl. Dan. (1780).
*Vaucheria aquatica* Lyngb. ('19).
*Hydronema* Carus ('23).
*Leptomitus prolifer* Ag. ('24).
*Saprolegnia capitulifera* Braun ('51).

Exsic.: Algues de la France, 238 (*A. prolifera*).
Rabh., Algen Sachsens, 242 (*do.*).

Hyphæ usually stout, sometimes slender. Zoösporangia formed from their swollen apices, usually thickest near the middle, *i. e.*, fusiform; the later ones arising on lateral branches from below the basal walls of the earlier ones, their successive formation resulting in a sympodial thread with apparently lateral sporangia. Zoöspores ovate or pyriform, at least sometimes, and probably always, apically biciliate, escaping by a single, usually terminal, mouth formed at the apex of a distinct papilla, and immediately becoming encysted and aggregated into a hollow sphere; after resting, swarming a second time in the laterally biciliate form; finally encysting again and germinating. Oögonia terminal or intercalary, one- to many-spored. Antheridia seldom wholly absent, often always present.

## *Key to recognized Species.*

| | | |
|---|---|---|
| *a.* | Oögonia with pitted walls | *b.* |
| | Oögonial walls not pitted | *c.* |
| *b.* | Plants diclinous | *A. prolifera.* |
| | Plants androgynous | A. AMERICANA. |
| *c.* | Oögonia with smooth walls | *d.* |
| | Oögonia with spiny walls | *i.* |
| *d.* | Plants strictly diclinous | A. OBLONGATA. |
| | Plants at least partly androgynous | *e.* |
| *e.* | Oöspores averaging ten or more | *f.* |
| | Oöspores averaging five or less | *g.* |
| *f.* | Oögonial branches short; oöspores excentric | *A. DeBaryana.* |
| | Oögonial branches long; oöspores centric | A. POLYANDRA. |
| *g.* | Oöspores over $40\mu$ in diameter; antheridial branches much branched | A. MEGASPERMA. |
| | Oöspores less than $40\mu$ in diameter; antheridial branches rarely branched | *h.* |
| *h.* | Oögonia usually apiculate; antheridial branches oftenest from the main hypha | A. APICULATA. |
| | Oögonia not apiculate; antheridial branches always from the oögonial branches | A. RACEMOSA. |
| *i.* | Antheridia on at least some oögonia | *k.* |
| | Antheridia wholly absent | *o.* |
| *k.* | Oögonia usually lateral at the ends of recurved branches | *A. recurva.* |
| | Oögonia terminal or intercalary, on straight branches | *l.* |
| *l.* | Oögonia globular; antheridia on each one | *m.* |
| | Oögonia oftenest elliptical; antheridia not on all | *n.* |
| *m.* | Oöspores averaging less than five; antheridial branches very short | A. RACEMOSA var. STELLIGERA. |
| | Oöspores averaging more than five; antheridial branches long | *A. oligacantha.* |
| *n.* | Oöspores 3–12, always globular | A. PAPILLOSA. |
| | Oöspores 1–3, often elongate | *A. spinosa.* |
| *o.* | Oögonia with rather sharp spines; oöspore single | *A. stellata.* |
| | Oögonia with blunt spines; oöspores one to three | A. CORNUTA. |

### *Achlya prolifera* (Nees ab E.) DeBary ('52).

Ill.: DeBary, '52, Pl. VII, Figs. 1–28.
DeBary, '81, Pl. II, Figs. 1, 2, and IV, 1–4.

This is the commonest European species, but it is doubtful if it has been seen in this country. Either it or the almost equally common *A. DeBaryana* appears very frequently in cultures, there. It is clearly distinguished by the abundantly pitted walls of its oögonia, which resemble those of the next species, and by its numerous and long antheridial branches of diclinous origin. Fungi reported under this name in American catalogues have belonged probably to the next or to other species.

From the fact of its abundance this species is rather more likely than any other to have been the one which Nees studied and called *A. prolifera*, although we have no means of knowing if this is actually the case. Under these circumstances there was no obligation to continue the name, but DeBary has chosen to do so by restricting it to this species; and, since it is the first name applied to the species, definitely recognized as such, and has been applied to no other recognizable species, it must stand. It is true that DeBary did not clearly characterize the species in the modern sense until 1881; yet in his earlier paper ('52) he described the pitted — or, as he then thought, perforated — walls of the oögonium; and as this is the only known European *Achlya* of that character, his description sufficiently marks the species, and the earlier date should be quoted for it.

### ACHLYA AMERICANA sp. nov.

Ill.: *Pl. XVIII, Figs. 69–73* (also on Pls. XIV–XVI).

Hyphæ stout, not very long. Zoösporangia very abundant, rather short and thick, slightly fusiform. Oögonial branches short, erect, racemosely arranged on the hyphæ. Oögonia terminal and globular, or rarely intercalary, their walls much pitted. Antheridial branches numerous, branching, arising from the main hyphæ between and near the oögonial branches. Antheridia very numerous, cylindric or somewhat clavate. Oöspores from one to fifteen in an oögonium, usually five to nine, excentric, their average diameter about 22$\mu$.

Massachusetts—Amherst: Pennsylvania—Philadelphia, *Keller:* Alabama—Auburn, *Atkinson:* Louisiana—St. Martinville, *Langlois.*

It is rather remarkable that our most abundant member of this genus, and indeed of this family, so far as the writer's observations go, while closely resembling the two commonest European species, combines their characters in a peculiar manner. Like *A. prolifera*, our form has oögonia with abundantly and invariably pitted walls; but, like *A. DeBaryana*, its antheridial branches are of androgynous origin; and, like both, its oöspores are of excentric structure. The pits of the oögonial walls are not conspicuous as in the *Saprolegniæ* of the *ferax* group, although they are usually of considerable size; but treatment with the chloroiodide of zinc always brings them out, as numerous transparent areas in the elsewhere deeply colored membrane. The antheridial branches are not so long nor so luxuriant as those of *A. DeBaryana*, as figured by DeBary ('81). They usually arise quite near the oögonial branches, very rarely even from the latter, which is said by DeBary never to happen in the last-named species; and the antheridia are rather shorter and envelop the oögonia less than is the case with the other.

These rather slight, but very constant, differences seemed at first to invalidate the distinction between the species called by DeBary *A. prolifera* and *A. polyandra*, and to indicate that they, with the present, are forms of a single variable species. But the very positive statement of so reliable an observer as DeBary as to the constancy of the characters of his two forms,* and the abundant evidence of repeated cultures from widely separated sources of the fixity of the present one, have left no alternative but to consider the three as distinct, though closely related, species, forming a series whose middle member is our American representative, and which may be termed the *prolifera* group.

I have met with this species in no less than twenty cultures from clean waters of every description, and from various parts of the country. It is the form referred to by the writer in an earlier note ('91) as "a form related closely to *A. polyandra* (perhaps that species);" and is that in which I first convinced myself of the presence of cilia on the escaping zoöspores of *Achlya*.

### *Achlya DeBaryana* nom. nov.

Syn.: *A. polyandra* DeBary ('81).

Ill.: DeBary, '81, Pl. IV, Figs. 5–12.
Ward, '83, Pl. XXII, Figs. 1–14.

This is, as already stated, one of the commonest European species, but it has not been recognized in America. It has smooth, unpitted oögonia and long, branched

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* I am indebted to Prof. Alfred Fischer, of Leipzig, who has had the opportunity of studying DeBary's material, for a full confirmation of that author's statements concerning these species.

antheridial filaments of androgynous origin, but agrees very closely in other respects with the two preceding species. As above indicated, it is the *A. polyandra* of DeBary, but it is clearly not the species to which that name was given earlier by Hildebrand ('67). DeBary appears to have believed that his species was that intended by Hildebrand; but, as will be fully shown later, this is not the case. And, since Hildebrand's species was pretty carefully described, it is perfectly recognizable. Hence the name *A. polyandra* belongs to it alone, and DeBary's species is left without a name. I therefore propose for the latter the name *A. De Baryana*, in honor of the profoundest student of the *Saprolegniaceæ*, to whom so large a part of our knowledge of the family is due.

### ACHLYA MEGASPERMA sp. nov.

Ill.: *Pl. XVIII, Figs. 74–77.*

Hyphæ stout, long. Zoösporangia thick, fusiform, freely developed. Oögonial branches short and straight, racemosely arranged. Oögonia terminal, globular, with smooth and unpitted walls which are strongly thickened. Antheridial branches often arising near the oögonial branches, but apparently never from them, much branched, often producing no antheridia. The latter absent from many oögonia, from one to several on others, short-clavate. Oöspores two to eight, commonly four to six, in an oögonium, centric, very dark when young, their average diameter 45$\mu$.

Massachusetts—Amherst.

Cultures from *Spirogyra*, dead leaves, etc., taken from a boggy spot by a small brook, are the only ones which have yielded the present well-marked species. The sporangia recall, in form and abundance, those of *A. Americana*, but the hyphæ are rather stouter and more vigorous than in that species. The very thick-walled oögonia, often without antheridia, and the very large oöspores, the largest known in this family, sometimes exceeding 50$\mu$ in diameter, distinguish it clearly from any other form. The thickening of the oögonial wall is not perfectly even, but its inner surface is somewhat irregular (Fig. 77) from unequal deposits of material. The protoplasm of the young oögonia and the oöspheres formed from it is very dense and dark colored, surpassing in this respect even that of *A. apiculata*. The plant is androgynous, but many of the smaller branches, which resemble in every other respect antheridial branches and strikingly suggest those of *A. DeBaryana*, fail to develop antheridia, and remain unattached to oögonia. Branches which do bear antheridia are otherwise similar to these. The antheridia which attach themselves to a given oögonium may or may not arise from the same hypha with it, though such is perhaps more often the case.

The precise systematic position of the species is perhaps open to discussion, but it presents points of resemblance and probable relationship with both the last and the following species.

### ACHLYA POLYANDRA Hildeb. ('67).

Syn.: *A. gracilipes* DeBary ('88).

Ill.: Hildebrand, '67, Pl. XVI, Figs. 7–11.
DeBary, '88, Pl. X, Figs. 2 and 6.
*Pl. XVIII, Figs. 78–81.*

Hyphæ stout, long. Zoösporangia often not abundant, secondary ones rare, nearly cylindrical. Oögonial branches usually very long and often recurved at the tip, racemose. Oögonia terminal, globular, with smooth and unpitted walls. Antheridial branches arising chiefly from the oögonial branches not far from the oögonia, often branched. Antheridia one to several on each oögonium, short-clavate. Oöspores five to twenty-five, usually ten to fifteen, in an oögonium, centric, their average diameter 27$\mu$.

Massachusetts—Amherst. Europe.

First obtained in spring from Algæ from a temporary rain-pool in a depression in a grassy field, this species appeared later in a culture from *Confervæ* and *Vaucheriæ*, taken from a running brook. Its numerous oöspores, very long oögonial branches, usually recurved at their tips, with the branched antheridial threads arising from them and bearing small and short antheridia, distinguish it from related forms. It appears to be rare with us, as I have never seen it from any other locality than Amherst, and only twice there.

It is especially interesting as having been the subject of a misunderstanding which has led to a confusion in synonymy that I have here attempted to correct. It was undoubtedly this species which Hildebrand described ('67) as *A. polyandra.* As has been already pointed out, DeBary gave the same name ('81) to a distinct species which he recognized as differing from Hildebrand's description, but thought to be probably his species. At the time of the completion of the paper quoted, DeBary had probably never seen this form, as his later paper ('88) states that he first obtained it in January of 1881, the year of the publication of the earlier one.

And while he did study it, he failed to notice its correspondence with Hildebrand's figures and description, and therefore named it anew *A. gracilipes.* But no one who will carefully compare the figures given by both authors will, I think, seriously question that they represent the same species. Again, Hildebrand states that secondary sporangia are not produced in his *A. polyandra*, a statement that DeBary ('81) disputes as untrue for his *A. polyandra.* But in his description of *A. gracilipes* ('88), DeBary says that secondary sporangia are only sparingly developed, a statement which I can corroborate for American specimens. The two descriptions agree in all other essential points, so far as they are comparable; and the evidence seems completely satisfactory that the correct synonymy of this distinct species is as above given.

The species shows as many points of affinity, perhaps, with *A. DeBaryana* and *A. megasperma* as with any others, but differs from them too widely to permit us to suppose any very recent common ancestry.

### ACHLYA APICULATA DeBary ('88).

Ill.: Ward, '83, Pl. XXII, Figs. 15, 16.
DeBary, '88, Pl. X, Figs. 3-5.
*Pl. XIX, Figs. 82-86, and XV, 26, 27.*

Hyphæ stout, often long. Zoösporangia fusiform, abundant. Oögonial branches somewhat elongate, usually hooked or recurved, racemose. Oögonia terminal, globular or oval, oftenest with a distinct apiculus, rarely intercalary, their walls smooth and unpitted. Antheridial branches rather stout, mostly unbranched, from near the base of the oögonial branch, or sometimes from that branch. Antheridia one to several on each oögonium, short-clavate. Oöspores one to ten, commonly three to five, in an oögonium, centric, their average diameter about 36μ.

Massachusetts—Amherst: Alabama—Auburn, *Atkinson.* Europe.

So far as Amherst is concerned, this species is the most abundant after *A. Americana.* It has appeared in several cultures from various pools and ditches, and is not to be confounded with any other species. Its sporangia are often more strikingly fusiform than those of most *Achlyæ*, as is well shown in Ward's figures ('83) and in our Fig. 82. The apiculate oögonia which contain, when young, a very opaque, dark-colored protoplasm, and, when old, a few large oöspores, are very characteristic and easily recognized. The oöspores are surpassed in size and opacity only by those of *A. megasperma*, and may reach, in extreme cases, a diameter of rather more than 40$\mu$. I have not observed the tendency towards the excentric type of oöspore said by DeBary to be sometimes shown by this species in the one-sided position of the oil-globule.

This plant shows some striking affinities with *A. megasperma* and *A. polyandra*; and, while in some respects intermediate between them, seems to take the position here given it with less violence to all considerations.

### ACHLYA OBLONGATA DeBary ('88).

Ill.: DeBary, '88, Pl. X, Figs. 7–9.
*Pl. XIX, Figs. 87–89.*

Hyphæ stout. Zoösporangia slightly fusiform, not abundant. Oögonial branches short or rarely somewhat elongate, straight, racemosely arranged. Oögonia occasionally intercalary, usually terminal, and elliptical, ovate, or obovate, rarely globular, with smooth, unpitted walls. Antheridial branches slender, of strictly diclinous origin, sometimes branched. Antheridia on every oögonium, numerous and small, short-clavate. Oöspores from one to twenty, usually seven to nine, in an oögonium, centric, their average diameter about 27$\mu$.

Massachusetts—Amherst: Louisiana—St. Martinville and Bayou Tortue, *Langlois*. Europe.

The elongate oögonia and diclinous hyphæ readily separate this type from all other *Achlyæ*, no other diclinous species being known except *A. prolifera*. It has occurred in cultures from Mill river, in Amherst, and from the aquatic room of the Plant-house of the Massachusetts Agricultural College, as well as in two cultures from Louisiana. The oögonia, which are typically rounded at their apices, show a tendency to a pointed form in some Louisiana specimens (Fig. 88); while in all cultures some of them are of a distinctly globular form, especially such as terminate principal hyphæ.

The oöspores commonly do not occupy the whole interior of the oögonium, but are collected into a group at one side, leaving an empty space. I do not, however, find them "viel kleiner als die aller Verwandten," as they are said by DeBary ('88) to be.

In the form and size of its antheridia and the delicacy of its antheridial branches as well as in its strict dicliny, the species strongly recalls *S. diclina*, but the resemblance goes no further.

### Var. GLOBOSA var. nov.

Ill. *Pl. XIX, Figs. 90, 91.*

Oögonial branches very short; oögonia globular; oöspores reaching twenty-five in number, averaging ten to fifteen; otherwise as in the type.

Pennsylvania—Philadelphia, *Keller:* Alabama—Auburn, *Atkinson.*

While not sufficiently different to be considered specifically distinct, this is certainly a well-defined variety of *A. oblongata*, marked by the very constant distinctions above indicated. It has been received from two widely separated localities, and appears to remain constant in culture. The oögonia are commonly larger than in the type and the space unoccupied by spores is much more marked (Fig. 90), sometimes amounting to more than half of the cavity. The antheridia correspond completely with those of the type, and furnish the best grounds for regarding the differences as of only varietal value.

This species shows no marked affinity with any other single species of *Achlya*, and its insertion at any particular point in the series is comparatively arbitrary. No real indication of affinities is possible in a linear arrangement of these species.

### ACHLYA RACEMOSA Hildeb. ('67).

Syn.: *A. lignicola* Hildeb. ('67).

Ill.: Hildebrand, '67, Pl. XV, Figs. 1–9, and XVI, 1–6*a*.
Cornu, '72, Pl. I, Figs. 2–8.
*Pl. XIX, Figs. 92–95.*

Hyphæ robust. Zoösporangia nearly cylindrical, sometimes tapering. Oögonial branches racemosely arranged, short and straight. Oögonia globular, their walls smooth and unpitted, somewhat irregularly thickened within, brownish-yellow when old. Antheridial branches very short and simple, arising from the oögonial branches near the basal walls of the oögonia, either above or below them. Antheridia one or two, rarely three or four, to each oögonium, short-clavate, usually bent, and applied by their apices to its wall. Oöspores one to ten, commonly two to six, in an oögonium, centric, their average diameter about $25\mu$.

Massachusetts—Amherst. Europe.

The typical form of the species, which was studied by Hildebrand, has appeared in two cultures in Amherst, one from dead leaves and slime from the outlet of a spring, and the other from a few *Ulothrichaceœ* taken from an open cask sunk in the soil of a pasture and apparently filled only by rains. It does not seem to be common. The species is readily recognized by the very characteristic antheridia, which are quite unlike those of any other species. The color of the old oögonial wall and its irregular thickening are also constant features. At the points of application of the antheridia hardly any secondary thickening occurs, so that it remains thin there.

There can be no doubt that Hildebrand's *A. lignicola* is merely a depauperate form of the present species, probably due in part to its growth on vegetable remains. There seems to be no reason for giving it even varietal rank. But we may distinguish clearly the

### Var. STELLIGERA Cornu ('72).

Syn.: *A. racemosa* var. *spinosa* Cornu ('72).
*A. colorata* Pringsh. ('82).

Ill.: Hine, '78, Pl. VI, Figs. 1–14.
Pringsheim, '74, Pl. XIX, Figs. 1–15; XXI, 1–3, 13; and XXII, 1–3.
Pringsheim, '82, Pl. XIV, Figs. 12, 15–31.
Pringsheim, '83b, Pl. VII, Figs. 10–20.
*Pl. XIX, Figs. 96–98.*

Oögonial walls more or less abundantly producing short, rounded outgrowths, more deeply colored when old. Oöspores very rarely exceeding five in an oögonium. Otherwise as in the type.

Massachusetts—Amherst and Northampton: New Jersey—Glassboro', *Keller:* New York—Ithaca, *Hine:* Louisiana—Bayou Tortue, *Langlois.* Europe.

This form seems much more abundant with us than the type. It was first recorded as American by Hine ('78); for although it was not definitely identified by him, his figures are unmistakable. I have observed it in cultures from three different sources in Amherst and its vicinity, including a swamp pool, a fish hatchery, and a river; also from a cedar swamp in New Jersey and from a Louisiana bayou. Though the degree of development of the spines may vary considerably in different specimens from the same culture, I have never seen a wholly smooth oögonium in a culture of the spiny form, or a spiny one among those of the typical form. And it is this fact which has seemed to indicate the propriety of characterizing the spiny form as a distinct variety. The two spiny varieties named by Cornu ('72) are apparently based on specimens with the spines respectively more and less developed; and, in the absence of evidence to the contrary, must be regarded as representing extremes of development within the limits of a single variety. The name STELLIGERA has been chosen of the two used by Cornu, to avoid confusion with *A. spinosa* DeBary, which is a very distinct species, in spite of the fact that it is quoted in Saccardo's *Sylloge* ('88) as a synonym of *A. racemosa* var. *spinosa* Cornu.

Besides the spiny oögonia and the fewer oöspores, one observes that in this variety the antheridial branches are, on the whole, even shorter than in the type-form, and more frequently arise from the wall of the oögonium itself than in the latter.

In February, 1891, I received, through Dr. J. B. Paige, of the Massachusetts Agricultural College, some trout eggs from the Northampton fish hatchery, which were evidently attacked by a fungus of this family, and were dead. The hyphæ failed to develop sexual organs, but fresh cultures, obtained by throwing flies into the vessel containing them, produced a new crop, bearing the sexual organs of this form. I was unable to visit the hatchery, but am informed that it proves necessary to remove dead eggs very frequently, since the infection spreads rapidly, and all the eggs in the hatching trays are killed unless this is done. After the eggs are hatched, the young fry appear not to be injured by the fungus. If this be true, the present species would seem to possess less parasitic capacity than the fungus of the salmon disease. It is probable that, in case of the eggs, the fungus can attack only the non-living egg-membranes, and that the death of the living cells of the egg is an indirect and not a direct result of its attack.

This variety may represent a transitional form between some smooth and spiny species of *Achlya*, not only as regards their oögonial structure, but also in the reduction of the antheridial branches, which is carried even to their entire disappearance in some spiny species.

## *Achlya oligacantha* DeBary ('88).

Ill.: DeBary, '88, Pl. X, Fig. 1.

The present species has delicate hyphæ which bear globular oögonia with rather few spines, and commonly four to eight oöspores each. Antheridia are developed on all the oögonia from rather elongate, simple branches of androgynous or diclinous origin. It has been observed by DeBary in a single culture from Baden, but not yet elsewhere. It may be regarded as representing a spiny form of the *polyandra* type, and in this respect differs from the spiny species to be described, which do not resemble closely any of the smooth-walled species, but constitute a distinct group of forms.

### ACHLYA PAPILLOSA sp. nov.

Ill.: *Pl. XX, Figs. 99–102.*

Hyphæ rather slender, long. Zoösporangia sparingly developed, cylindrical, little larger than the hyphæ. Oögonia terminal on main threads or on short lateral branches, or sometimes intercalary, oval or ovate, rarely globular, thickly studded with short, blunt, wart-like outgrowths of their unpitted walls, often with a marked apiculus. Antheridial branches usually developed with each oögonium, fine and branching, arising near it from the main thread, or rarely from the oögonial branch. Antheridia imperfectly formed. Oöspores as many as twelve in an oögonium, oftenest four to six, centric, their average diameter about 25$\mu$.

Massachusetts—Amherst.

This plant, which seems to be sufficiently distinct from previously described species, has been obtained in several cultures, but from only a single source; namely, the very prolific mossy pool in Amherst, already mentioned. It may be recognized by its long hyphæ, finer than those of most *Achlyæ*, and its oögonia with warty, rather than spiny, walls, and several oöspores in each. I have never seen well-differentiated antheridia or fertilization-tubes, although the ends of the antheridial branches are applied to the oögonia.

While bearing no near resemblance to any species heretofore figured, this plant may be somewhat closely related to the next, if the latter is well founded.

### *Achlya recurva* Cornu ('72).

So far as the incomplete account published by its author enables one to judge, this is a distinct species from the last, and is separated by its longer and recurved oögonial branches, on which the oögonia are usually borne laterally, and by its better developed antheridia, often digitately branched. Aside from the original observations of its author ('72), this species has been recognized only by Hartog ('88).

### *Achlya spinosa* DeBary ('81).

Ill.: DeBary, '81, Pl. IV, Figs. 13–18.

Its author's latest description of this species ('88) does not fully agree with his earlier figures ('81), especially in that he states that the oögonia are never intercalary, while he has figured several such. It should be, however, readily enough recognized by the usually barrel-shaped oögonia, with numerous blunt, and often broad or even forked, outgrowths, each containing one or two oöspores which often take an elliptical form corresponding to that of the cavity of the oögonium. The principal hyphæ commonly produce very abundant closely set, short, lateral branches that give to the whole plant a densely woolly appearance; and reproductive organs are often produced only when these branches reach a new food-supply and give rise to fruiting hyphæ. The species was obtained by DeBary from a lake in the Black Forest, known as the "Titisee."

### ACHLYA CORNUTA Archer ('67).

Ill.: Archer, '67, Pl. VI, Figs. 2–6.
*Pl. XX, Figs. 103, 104.*

Hyphæ of medium size, short. Zoösporangia rare, cylindric. Oögonial branches rarely long, straight or flexuous, racemosely arranged. Oögonia terminal, globular or elliptical, densely beset with rather long, blunt outgrowths of their unpitted walls, the apical one often larger and forming an evident apiculus. Antheridial branches and antheridia wanting. Oöspores from one to four in an oögonium, globular or slightly flattened, centric, their average diameter about 29$\mu$.

Massachusetts—Amherst. Europe.

The same culture which yielded *A. megasperma* for the first time contained a small amount, all I have seen, of this form. It has been referred with some doubt to Archer's species, since it fails to show at all a feature which one would suppose, from that author's account and figures, to be very characteristic of his plant; namely, the development of several oögonia in a series from a single hypha. In other respects, however, it corresponds too closely with his description to justify one in regarding it as distinct. Archer saw no sporangia, probably not, as he thought, because he found it too late, but because of their rarity. In species which produce sporangia abundantly, one can always find empty ones on plants with mature oöspores. In the limited material at my disposal, I have been able to find but a single one, and that only long after it was emptied. From below its base arose a branch bearing an oögonium. This, so far as it goes, supports Archer's conclusion that the plant is an *Achlya*, which seems almost certainly correct. The oögonial branches sometimes show the incurving mentioned by Archer, and are often less definitely bent. This writer states that an oögonium may contain as many as eight or ten oöspores; but I have never seen more than four, and his figures show no more than three. He describes no special antheridial branches, but says that the antheridia are like those of *A. dioica* Pringsh. As these latter are not antheridia at all, one would expect to find, as is the case with American specimens, that the species has no true male organs. As will be seen from the figures, the spines could hardly be more closely set, and their form is more cylindrical than conical.

This and the next species seem to be closely related, the more so if the American form here described proves to be more typical than Archer's.

### *Achlya stellata* DeBary ('88).

Ill.: DeBary, '88, Pl.X, Figs. 10, 11.

Like the last, to which, indeed, it seems almost too similar, this plant has no antheridia. Its globular or elliptical oögonia are covered by rather less numerous spines that are shorter and sharper, therefore more conical, than those of *A. cornuta.* The oöspores are always single and sometimes correspond in form with the cavity of the oögonium, instead of being always globular. It is known only from a single locality near Göttingen.

### Species inquirendæ.

*Achlya contorta* Cornu ('72, Pl. I, Figs. 9–15), with smooth oögonia, containing on an average eight oöspores, and borne on long, spirally twisted branches with peculiar local swellings, and with branched cylindrical antheridia; and *Achlya leucosperma* Cornu ('72), with antheridia similar to the last, and oögonia with two-pitted walls and light-colored oöspores, have been studied only by their author, whose descriptions are too imperfect to determine their position. While they may prove to be distinct species, more definite and complete information concerning them is much needed.

*Achlya dioica* Pringsh. ('60, Pl. XXIII, Figs. 1–5), should be written as a synonym, probably of some species already described; but as the oögonia were not mentioned or figured, it is impossible to say to what species it belongs. The name was given to some hyphæ said by the author to be those of an *Achlya,* which were attacked by a Chytridiaceous parasite, probably that since described by Cornu ('72) as *Woronina.* The cysts of the parasite were supposed to be the antheridia of the fungus. This belief, which also led to the similarly erroneous application of the name *Saprolegnia dioica*, was based on the supposed necessity for the existence of antheridia and a sexual process in these plants.

*Achlya Nowickii* Racib. (Przyrodnik [The Naturalist] V, 327; 1884) may be a good species, but I have not been able to examine the original description.

*Achlya penetrans* Duncan (Proc. Roy. Soc. London, XXV, 238; 1876) is probably a boring Siphonaceous alga.

## **Aphanomyces** DeBary ('60).

Hyphæ very slender and delicate, little branched, forming a nebulous film over the substratum. Zoösporangia formed from their unswollen ends, often a hundred or more times as long as broad; secondary ones not abundant, formed by cymose branching. Zoöspores cylindric-fusiform, cilia not yet observed, formed in a single file in the sporangium, and escaping slowly by a terminal mouth which is formed without the preliminary development of an oral papilla; immediately becoming encysted and aggregated into a hollow rounded group; after resting, swarming in the laterally biciliate form; finally encysting again and germinating. Oögonia usually terminal and one-spored. Antheridia commonly present.

### *Key to established species.*

| | | |
|---|---|---|
| *a.* | Parasitic on *Zygnemaceæ;* oögonia spiny | *Aph. phycophilus.* |
| | Saprophytic | *b.* |
| *b.* | Oögonia quite smooth; antheridia always present | APH. LÆVIS. |
| | Oögonia roughened or spiny | *c.* |
| *c.* | Spines large and prominent; antheridia always present | *Aph. stellatus.* |
| | Spines small or reduced to mere roughnesses; antheridia often absent | APH. SCABER. |

### APHANOMYCES LÆVIS DeBary ('60).

Ill.: DeBary, '60, Pl. XX, Figs. 17, 18.
*Pl. XX, Figs. 105–107.*

Zoösporangia very long and slender. Oögonia terminal on short lateral branches, globular, with entirely smooth walls. Antheridia abundantly developed on all oögonia, large, clavate-cylindric, on short branches of androgynous or diclinous origin, sometimes even from the oögonial branch. Oöspores single, globular, centric, 20 to 22$\mu$ in diameter.

Massachusetts—Amherst. Europe.

The present species appeared in a single culture from moss and Algæ (chiefly *Tolypothrix*) from the mossy pool frequently mentioned, which had stood in a jar in the laboratory for several months. It is readily distinguished by its smooth oögonia from all other species except the smoothest forms of *Aph. scaber*, from which it differs in its large and numerous antheridia and larger oöspores. The fertilization tubes are plainly developed and the species seems in all respects to represent the most primitive form of the genus.

It is worthy of remark that, although the genus was described more than thirty years ago, no other species than the four then characterized have yet been recognized.

### *Aphanomyces stellatus* DeBary ('60).

Ill.: DeBary, '60, Pl. XIX, Figs. 1–13.
Sorokine, '76, Pl. VII.

Distinctly marked by its oögonia with large, blunt spines or warts, and its well-developed antheridia, which seem to be present on every oögonium, combined with its strictly saprophytic habit. DeBary states that in rare cases an oögonium may contain two oöspores, the only deviation from the one-spored condition known to occur in the genus.

This species has been studied by Sorokine ('76), as well as by its author, and is probably common in Europe, and perhaps also in America, though I have not yet met with it. It seems to be similar to the last species except in the spiny character of its oögonia, a condition towards which, whatever its significance, there is a distinct tendency in several groups of species in this family.

### *Aphanomyces phycophilus* DeBary ('60).

Ill.: DeBary, '60, Pl. XX, Figs. 19–24.

Although the zoösporangia and sexual organs were not observed by DeBary on the same plant, there seems to be little doubt that this species is properly placed in the present genus. Its oögonia are the largest of the genus and have relatively smaller and sharper spines than the last species, while its antheridia are well developed and always present. But its chief peculiarity lies in its parasitism upon Algæ, in which it is unique among *Saprolegniaceæ* and recalls the related genus *Pythium.* Its host-plants are *Spirogyra* and *Zygnema,* whose cells it rapidly destroys. It has been observed as yet only in Europe. While structurally distinct from the last species, and shown by DeBary to be also physiologically so, this must be regarded as a plant of the same type, which has acquired the parasitic habit.

### APHANOMYCES SCABER DeBary ('60).

Ill.: DeBary, '60, Pl. XX, Figs. 14–16.
DeBary, '81, Pl. VI, Figs. 30–36.
*Pl. XX, Figs. 108–111.*

Zoösporangia very long. Oögonia small, terminal on short branches, or on main hyphæ, globular; their walls with numerous short spines or prominences, or merely irregularly roughened. Antheridia on branches of androgynous or diclinous origin, small, not on all oögonia. Oöspores single, globular, centric, 16 to 18$\mu$ in diameter.

Massachusetts—Amherst. Europe.

The spiny form of this species (Figs. 108, 109) appeared in a single culture from dead leaves and slime taken from a ditch in Amherst, and the merely rough form (Figs. 110, 111) was obtained later from a mass of *Spirogyra* which grew in the same ditch, at a point a few rods away from the source of the first.

Both forms agree closely except in the roughnesses of the oögonia, which may be very slight or may take the form of short and rather sharp spines. But the species is always known by the smaller oöspores and by the reduced size and number of the antheridia. These latter are wholly wanting on half or even more of the oögonia. In my few cultures they have been rather less abundant in the smoother than in the spiny form, and the two extreme types of oögonia have not appeared together. It may therefore prove justifiable to regard the smoother form as a distinct variety, but further evidence is needed on this point. The character of the present species points to the conclusion that it should be regarded as the least typical of the genus, representing a degeneration in both sexual organs from the type of *A. stellatus.*

### *Thraustotheca** gen. nov.

Hyphæ stout, branching. Zoösporangia formed from their swollen ends, clavate; the later ones formed by sympodial branching. Zoöspores encysting within the sporangium at once after their formation, somewhat polyhedral from pressure, but with distinct membranes; soon set free by the breaking up of the very fragile sporangial wall, and then escaping from their cysts to swarm in the laterally biciliate form; finally encysting again and germinating. Oögonia several spored, with abundant antheridia.

### *Thraustotheca clavata* (DeBary).

Syn.: *Dictyuchus clavatus* DeBary ('88).

Ill.: Büsgen, '82, Pl. XII, Figs. 1–8.
DeBary, '88, Pl. IX, Fig. 3.

This, the only species of the genus yet known, strikingly resembles *Achlya DeBaryana* in its sexual organs, having similar long and branching antheridial threads and smooth oögonia with excentric oöspores. But its short, clavate sporangia and the peculiarities in the development of its zoöspores separate it widely from the latter. It is known only from near Strassburg, Germany.

A careful comparison of the characters of this species, as drawn from the accounts of Büsgen ('82) and DeBary ('88), with those of species of *Dictyuchus*, taken from the American specimens studied by the writer, will furnish, it is believed, sufficient justification for its separation from the latter genus. An account of the differences on which the new genus is based will also be found in the discussion of generic relationships on a previous page. The close analogy of the sporangia of this plant with those of *Mucor* has already been pointed out by Solms-Laubach, to whom we owe the arrangement of incomplete fragments of DeBary's last paper ('88), and he has also hinted at the possibility of generic differences between this and the other described species of *Dictyuchus*. His suspicions are quite supported by the very different means adopted, in the two types, for the release of the zoöspores after their encystment within the sporangium. The species needs further study, especially with reference to the nature of the intermediate substance said to exist between the zoöspores within the sporangium.

## **Dictyuchus** Leitgeb ('68).

Hyphæ stout or slender, branching. Zoösporangia formed from their swollen ends, usually fusiform; the later ones formed in basipetal succession below the earlier,

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* *θραυστός*, fragile ; *θήχη*, a case.

or by sympodial branching, or in both ways on the same hypha. Zoöspores encysting within the sporangium at once after their formation, polyhedral from mutual pressure, the membrane of each face united with that with which it is in contact to form an apparently single wall; after a time escaping, each by a separate opening through the outer wall, and swarming in the laterally biciliate form; finally encysting again and germinating. Oögonia terminal or intercalary, one- or several-spored. Antheridia usually present.

## *Key to the known Species.*

*a.* Plants diclinous; oöspores single.................*b.*
Plants androgynous; oögonia several-spored.................*D. polysporus.*
*b.* Oögonia under 30μ in diameter, encircled by the antheridia.................*D. monosporus.*
Oögonia over 30μ in diameter, not encircled by the antheridia.................D. MAGNUSII.

### DICTYUCHUS MAGNUSII Lindst. ('72).

Ill.: Lindstedt, '72, Pl. I, Figs. 1–15.
*Pl. XX. Figs, 112–114.*

Hyphæ rather large. Zoösporangia cylindric or fusiform. Oögonia terminal on slender branches, globular, smooth-walled, unpitted. Antheridia cylindric or slightly clavate, on all oögonia, borne on slender branches of diclinous origin. Oöspores single, centric, about 25μ in diameter.

Massachusetts—Cambridge, *Trelease.* Europe.

Our knowledge of the occurrence of this species in America rests on the notes and preparations of Prof. Trelease, who obtained it in 1881 from water in the Botanic Garden, at Cambridge. It can be confounded only with *D. monosporus,* from which it differs in its somewhat larger oögonia and less coiled antheridial branches.

Lindstedt states that it is only in this species that the sporangia are formed from the hyphæ in basipetal succession, but it seems doubtful if this is strictly true, in view of certain observations to be mentioned later.

The definition of the present genus by its author was less restricted than that above adopted, which is essentially that of Lindstedt ('72), but seems, for reasons suggested in the discussion of the genus *Thraustotheca,* to be a more accurate and philosophical one.

### *Dictyuchus monosporus* Leitgeb ('69).

Ill.: Leitgeb, '69, Pl. XXII, Figs. 1–12; XXIII, 1–8.

Not yet known in America. Resembles the last species closely, but has smaller oögonia and short, coiled antheridial branches.

### *Dictyuchus polysporus* Lindst. ('72).

Ill.: Lindstedt, '72, Pl. II, Figs. 1–3; III, 1–7.

Distinguished by its large, globular, many-spored oögonia and its antheridial branches of androgynous origin, from all other described species of the genus. Not seen in America.

In one of my cultures of *Aph. scaber* there appeared hyphæ and sporangia of a species of *Dictyuchus.* A vigorous growth of it was readily obtained on fresh flies and kept up in successive generations for several months. In ordinary cultures in glass vessels, the sporangia are freely and normally produced both in basipetal series and by cymose branching. In cultures on slides in a moist chamber, one often sees sporangia lobed and forked in quite irregular fashion, like those figured by Leitgeb ('69) for *D. monosporus.* The plant seems slenderer and more delicate than *D. Magnusii* of Prof. Trelease's preparation, and is very probably not that species. It does not appear that either the basipetal development of sporangia or their forked shape can be regarded as of any specific value. In spite of repeated efforts to induce their development, the sexual organs of this plant have uniformly failed to appear, so that it is quite impossible to say what species it represents. After the formation of sporangia has begun to decline, the main hyphæ of a plant commonly send out a mass of fine lateral branches, themselves much branched and interlacing, which give to the whole culture a densely woolly appearance. These threads probably correspond to those which bear the sexual organs in *D. monosporus,* but, although readily kept alive and healthy for a long time, they remain persistently sterile. Gradually the later generations of the plant showed signs of degeneracy, and ultimately refused to yield normal plants.

Two or three cultures from various sources have produced a plant with slender hyphæ and sporangia of the *Dictyuchus* type, except that they contain only a single file of zoöspores, being cylindrical and little larger than the hyphæ. It is this form whose sporangium is shown in Fig. 16. I have never been able to find its sexual organs, and specific determination is, therefore, impossible.

## *Aplanes* DeBary ('88).

This genus represents the extreme result of the reductional tendencies observed in previous genera, in that both swarming stages are entirely suppressed. The zoöspores encyst within the sporangium and germinate there, producing germ-tubes which penetrate the sporangial wall and thus make their way into the surrounding water.

### *Aplanes androgynus* (Archer).

| | |
|---|---|
| Syn.: *Saprolegnia androgyna* Archer ('67). | Ill.: Archer, '67, Pl. VI, Fig. 1. |
| *Achlya Braunii* Reinsch ('78). | Reinsch, '78, Pl. XIV, Figs. 1–6. |
| *Aplanes Braunii* DeBary ('88). | DeBary, '88, Pl. IX, Fig. 2. |

The present very striking species would seem not to be rare in Europe, having apparently been met with by several investigators; but it is not known to be American. It is recognized by its several spored, barrel-shaped or spindle-shaped oögonia, with pitted walls, often formed in series from a hypha, and by its numerous antheridial branches arising just below the basal wall of each oögonium, even though it be from the sides of the next oögonium in the series.

Although it is not absolutely certain that the plants studied by Archer, Reinsch, and DeBary all belonged to the same species, there seems to be little doubt of the correctness of such a conclusion, in spite of the fact that Reinsch's account of the sporangia does not agree with DeBary's, and that Archer does not mention the pits of the oögonial wall. The overlooking of the latter would have been less remarkable twenty-five years ago than to-day; and Archer's failure to see the sporangia is readily explained by DeBary's statement that they are very rarely developed. Archer's arguments for placing his plant in the genus *Saprolegnia* are drawn wholly from analogy, and not from observation of the sporangia.

Reinsch's description of the sporangia suggests that he perhaps did not see those of the plant whose sexual organs he studied, but mistook for them those of a *Dictyuchus* which may have grown intermingled with the other. At all events, the agreement in the structure of the sexual organs has led DeBary to feel very sure of the identity of his plant with Reinsch's, but he seems to have overlooked the equally complete similarity of Archer's plant. It seems best, then, to consider all the names above quoted as synonyms; and, while retaining DeBary's generic name, the plant must bear the specific designation given it by Archer, since that is the older.

### *Subfamily Leptomiteæ.*

## **Leptomitus** Agardh ('24).

Syn.: *Apodya* Cornu ('72).

Hyphæ stout at the base, marked off at intervals by deep constrictions into distinct segments; branching abundant, dichotomous below, but often monopodial on the finer ultimate divisions; branches arising only from the acroscopic ends of the segments. Zoösporangia formed from swollen segments of the hyphæ which are cut off at the constrictions; the primary ones from apical segments, and later ones often several in basipetal succession. Zoöspores biciliate, monoplanetic (?), swarming separately. Oögonia and antheridia unknown.

### LEPTOMITUS LACTEUS (Roth) Ag. ('24).

Syn.: *Conferva lactea* Roth (1789).
*Saprolegnia lactea* Pringsh. ('60).
*Apodya lactea* Cornu ('72).
Exsic.: Rabh., Algen Sachsens, 587.

Ill.: Dillwyn, '09, Pl.
Pringsheim, '60, Pl. XXIII, Figs. 6–10; XXV, 1–6.
Pringsheim, '83b, Pl. VII, Figs. 1–9.
Büsgen, '82, Pl. XII, Figs. 9–15.
*Pl. XX, Figs. 115–118.*

Hyphæ rapidly decreasing in diameter with successive subdivisions; apical segments about 10$\mu$ in diameter and often forty times as long. Zoösporangia cylindrical, from slightly swollen segments, their mouths terminal or lateral. Zoöspores in a single file within them.

Massachusetts—Amherst: Connecticut—Bridgeport, *Holden.* Europe. Probably common everywhere.

This unmistakable form appears to be common enough in Amherst, and is undoubtedly so elsewhere in favorable situations. It prefers, as has been before intimated, waters which are somewhat, but not too strongly, polluted by organic substances. I first met with it on masses of decaying Algæ which had died and broken down in the vessel in which they had been kept. Afterwards it appeared in fly cultures from waters from the outlets of drains, containing decaying vegetable matter. It does not appear to flourish where active decay of animal substances is going on. In favorable places, it often forms very dense masses of closely felted threads, covering very large surfaces. Gœppert observed ('52) such a case in a small stream below a beet-molasses manufactory, near Schweidnitz, in Silesia. I have received from the herbarium of Prof. W. G. Farlow a specimen from a similar mass, collected in a stream, below a "tripe-house," at Bridgeport, Conn., by Mr. Isaac Holden.

The species is easily recognized by the regularly dichotomous branching and rapid reduction in size of its principal hyphæ, and by its cylindrical sporangia developed in basipetal succession. While the zoöspores ordinarily escape from the sporangia, they sometimes become encysted within them (Fig. 117). It is this fact, probably, which led Braun to state ('51) that the spores of *Leptomitus* are arranged in a row in the spore cases, and that "no active gonidia seem to occur."

The hyphæ of this plant are especially favorable for the study of the so-called cellulin grains. Frequently, when a sporangium is formed, its narrow connection with the next segment is closed by the occupation of the passage by one of these granules. This simple method of forming a cross partition is perhaps not very different in kind from that which occurs in the *Saprolegnieæ.*

### SPECIES INQUIRENDÆ AUT EXCLUDENDÆ.

Many so-called species of this genus have been described by early authors, and may be found catalogued by Kützing ('49), and in part by Saccardo ('88). The great body of them are merely sterile, submerged hyphæ of uncertain origin, and even to list them here would be useless. The only species which need be mentioned, and concerning which further information is desirable, are:

*Leptomitus Libertiæ* (Bory) Ag. ('24) [Exsic., Libert, Plantes Crypt. Ard., 97], placed doubtfully by Saccardo ('88) under *Saprolegnia.* The published description mentions no reproductive organs and I have not been able to examine Libert's *exsiccata.* So far as the description goes, the plant may belong to this family, but probably rather to the *Saprolegnieæ* than to the present subfamily.

*Leptomitus rubescens* DeBréb. [Exsic., Algues de la France, 306], and

*Leptomitus Doriæ* Ces. [Exsic., Rabh., Algen Sachsens, 575] are mentioned only in the quoted *exsiccatæ.* They will probably prove to be only sterile hyphæ.

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## **Apodachlya** Pringsh. ('83b).

Hyphæ slender throughout, marked off at intervals by constrictions into distinct segments; branching monopodial; branches arising from any part of a segment.

Zoösporangia from considerably swollen segments, renewed by sympodial branching. Zoöspores usually becoming grouped at the mouth of the sporangium, on escaping, rarely swarming separately; soon leaving their cysts and swarming; finally encysting again and germinating. Sexual organs known in but one species.

As Pringsheim has observed in one species ('83b), and Zopf in another ('88), that the zoöspores commonly escape after the manner of *Achlya*, there seems to be as good reason for the generic separation of the following species from *Leptomitus*, as for keeping *Saprolegnia* and *Achlya* distinct, and also since there are marked differences in the branching of the hyphæ and in the formation of secondary sporangia.

The species heretofore recognized are:

### *Apododachlya brachynema* (Hildeb.) Pringsh. ('83b).

Syn.: *Leptomitus brachynema* Hildeb. ('67). Ill.: Hildebrand, '67, Pl. XVI, Figs. 12–23.

Has hyphæ with short segments, and globular sporangia opening by short necks and often occurring in series. No sexual organs are known.

### *Apodachlya pyrifera* Zopf ('88).

Ill.: Zopf, '88, Pl. XXI, Figs. 1-21.

Has hyphæ with long segments, pyriform sporangia, developed singly and each opening by a distinct papilla, and large globular chlamydospores. Sexual organs have not been seen.

To these species it seems necessary to add:

### APODACHLYA (?) COMPLETA sp. nov.

Ill.: *Pl. XX, Figs. 119–121.*

Hyphæ slender, with rather long segments. Zöosporangia unknown. Oögonia terminal on branches of one or a few segments, each representing a swollen segment, globular, with smooth, unpitted walls. Antheridia formed from lateral cylindrical branches of one or two segments which arise from the slightly swollen apical part of the segment next below the oögonium, usually two from each. Oöspores oftenest five to seven, sometimes less or more, thick-walled when mature, centric, 18 to 20$\mu$ in diameter.

Louisiana—St. Martinville, *Langlois.*

This very interesting plant affords the first recorded instance of the occurrence of sexual organs among the *Leptomiteæ*, unless the imperfectly described *S.* (*Leptomitus*) *corcagiensis* of Hartog be such an example. The latter cannot, however, be the same form as the present one. This plant appeared in very limited quantity on a fly which had been thrown into an old and feeble culture of *Saprolegnia* sp., obtained by Rev. Mr. Langlois from a ditch in St. Martinville, La. The moribund condition of the culture when it was received caused these freshly added flies to decay so much that the development of other *Saprolegnieæ* was slight and unhealthy; but the few plants of this form were developed normally and seemed to find their surroundings congenial, indicating that it, like *L. lacteus,* is partial to polluted waters.

A very careful and detailed examination of the material failed to discover any sporangia, and it does not, therefore, certainly belong to the present genus. But, since the hyphæ are certainly not those of *L. lacteus*, but are slender throughout, branch monopodially from all parts of their rather long segments, and in general resemble strikingly those of *Apod. pyrifera,* it is placed provisionally here.

Its great interest lies, as before suggested, in its possession of well-formed sexual organs of peculiar and characteristic structure. The oögonia are globular and are formed by the swelling of the terminal segment of a branch. When young, they are filled by granular protoplasm which is entirely used up in the formation of the oöspheres, a fact which confirms our previous belief that these plants belong to the present family. The narrow connection between the oögonium and the next segment below it becomes quite solid, and the apical end of the latter segment is usually somewhat swollen and gives rise to the, commonly two, antheridial branches. The oöspores, when mature, are quite thick-walled and of uniform and moderately granular appearance (Fig. 120).

The antheridial branches are composed of one or two cylindrical segments each, and are at first uniformly filled with protoplasm and applied to the oögonium (Fig. 119). Later, a part of a segment may be cut off by a transverse wall (Fig. 120), and then apparently constitutes an antheridium. The part cut off in Fig. 120 will be seen to be quite empty, and similar cases are frequent; but I have never been able to recognize fertilization tubes homologous with those of the *Saprolegnieæ.* On the other hand, the whole segment may become nearly or quite emptied, as shown in the right hand branch in Fig. 121. The left hand branch in the same figure shows a condition observed in a number of instances, which is one of much interest. The limited material at hand did not permit extended observations as to its significance, but the facts appeared to be as follows in all of the several similar specimens observed. In the basal part of the branch there are formed, in a single row, several globular protoplasmic masses with distinct walls. The spaces around the individual spheres seem to be separated by faint false walls of protoplasmic substance, probably formed from the protoplasm of the segment. These spheres produce structures which can be compared to nothing but germ tubes in their appearacne and growth; and I have seen them in all stages from the beginning of their formation to the length shown in Fig. 121. They ordinarily grow towards the oögonium, but I have seen two of them, developed from two spheres contained in the same segment, directed away from it. In this last case they were in the lower segment of a branch of two segments whose upper member showed the same condition as that drawn in Fig. 120. While one's first inclination may be to regard these peculiar structures as specialized male cells which produce fertilization tubes of a different type from those of the *Saprolegnieæ*, yet the emptying of the apical parts of some branches, even of the same ones that contain the spheres, and the fact of the growth of their tubes away from the oögonium in one observed case, make it quite as probable that they are parasites in the antheridial branches. Yet if they are parasites, it is remarkable that they should not have been seen in other parts of the plant. I have not been able to observe what follows the contact of their tubes with the oögonium, not having seen them late enough in their history.

The general incompleteness of these observations, which bring up many interesting possibilities, can justify nothing more than the suggestion of some of these possibilities. The emptying of the separated apical parts of some branches without any evident formation of fertilization tubes needs further investigation; it is not impossible that this species may be shown to differ from the *Saprolegnieæ* which have been studied, in the occurrence of a truly sexual process. It is greatly to be hoped that some one may soon have the opportunity of studying abundant material of this plant.

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## EXPLANATION OF PLATES.

### *Plate XIV.*

Fig. 1. A fly attacked by *Saprolegnia* sp. × 2.

Fig. 2. Rhizoids of *S. mixta,* giving rise to an external hypha, *h.* × 130.

Fig. 3. Cut-off ends of hyphæ of *Saprolegnia* sp. repaired by the formation of a cellulose wall. × 200.

Fig. 4. Protoplasm and nuclei of a portion of an hypha of *A. racemosa.* × 940.
Picric-acid-Hæmatoxylin specimen; the protoplasm somewhat retracted from the walls by the action of the acid.

Fig. 5. Nuclear division in an hypha of *A. apiculata.* × 1400.
*a.* The nucleus, showing chromatin-mass, nuclear membrane, and the intermediate space.
*b.* The chromatin-mass has elongated with the rest of the nucleus.
*c.* The chromatin mass is dividing.
*d.* The nuclear membrane is formed between the daughter-nuclei, which have not yet separated. Corrosive-sublimate-Hæmatoxylin preparation.

Fig. 6. A bit of *L. lacteus,* showing monopodial branching and two cellulin granules, *c.* × 540.

Fig. 7. Two stages in the development of the zoöspores of *A. Americana,* showing only the base and tip of the sporangium. × 350.
*a.* The first separation fairly marked, at 11.10 A.M.
*b.* The "homogeneous" stage, at 11.23.

Fig. 8. A sporangium of *Saprolegnia* sp., with zoöspores in the act of escaping, some already out, *z.* × 540. Osmic-acid-anilin-violet preparation.

Fig. 9. Four zoöspores of *A. Americana* fixed at the moment of escape; from two sporangia, *a* and b. × 540. Osmic acid-anilin-violet preparation.

Fig. 10. Four sporangia of *A. Americana* successively developed by cymose branching, in the order of the figures *1* to *4*; the empty spore-membranes still adhering to two. × 200.

Fig. 11. The tip of a sporangium of *Aphanomyces* sp., with the head of spore-membranes, most of which have been vacated by the spores; showing a living spore, *z,* in its second form, its cilia not clearly visible, and a similar spore, *z′,* killed with iodine to show its cilia.
*a–i,* a series of stages in the development of a spore which germinated *in situ,* without the second swarming: *a,* at 10 A.M.; *b,* at 10.09; *c,* at 10.14; *d,* at 10.19; *e,* at 10.29; *f,* at 10.40; *g,* at 11; *h,* at 11.45; *i,* at 12 M. × 540.

Fig. 12. Two encysted zoöspores of *A. apiculata.* × 800. Corrosive-sublimate-Hæmatoxylin preparation.

Fig. 13. Beginning of the germination of a zoöspore of *A. racemosa,* after one division of the nucleus. × 940. Picric-acid-Hæmatoxylin preparation.

Fig. 14. Renewal of sporangia of *Saprolegnia* sp. by growth of new ones into the empty membranes of old ones. × 200.

Fig. 15. Empty, "nested," membranes of successive sporangia of *Saprolegnia* sp., the order of their development shown, *1 — 6.* × 200.

Fig. 16. A part of a sporangium of *Dictyuchus* sp.; showing several stages in the escape of the zoöspores, and a mature zoöspore, *z.* × 540.

Fig. 17. Branching of hyphæ below empty sporangia in *Aph. scaber.* × 540.

## *Plate XV.*

Fig. 18. Chlamydospores of *A. Americana.* × 200.
Fig. 19. Chlamydospores of *Achlya* sp. × 74.
Fig. 20. Germination of chlamydospores of *Achlya* sp. × 74.
Fig. 21. Origin of oögonium, *o*, and antheridium, *a*, from an hypha of *A. Americana.* × 200.
Fig. 22. A divided oögonial branch of *A. apiculata,* bearing three oögonia. × 200.
Fig. 23. A proliferous oögonium of *A. polyandra.* × 200.
Fig. 24. An oögonium of *A. Americana* which has reverted to the vegetative condition and given rise to new sexual organs. × 540.
Fig. 25. Antheridial branches of *A. Americana* terminated by oögonium-like swellings. × 350.
Fig. 26. Four stages in the development of the oöspheres of *A. apiculata; a,* the parietal layer still intact, the protoplasm accumulating into masses, at 11.50 A.M.; *b,* the parietal layer ruptured and withdrawn into the three distinct masses, at 12 M.; *c,* the separation of small portions from the main protoplasmic masses, at 12.10 P.M.; *d,* the reabsorption of these masses, at 12.18 P.M. × 350.
Fig. 27. A still later stage than 26, *d,* the oöspheres quite rounded off, at 12.23 P.M.; showing also the antheridial branches. × 350.
Fig. 28. An oögonium of *A. papillosa* which has reverted to the vegetative condition and produced three hyphæ with sporangia, one of them fully shown at *2.* × 200.
Fig. 29. Germination *in situ* of the oöspores of *A. Americana; a,* two spores with young germ tubes; *b,* one oöspore with a fully developed hypha and empty sporangium. × 540.

## *Plate XVI.*

Figs. 30–36. Cytology of the sexual organs of *A. Americana.* From Corros.-subl.-Hæmatoxylin preparations.
Fig. 30. Young oögonium with its central vacuole formed, its nuclei irregularly scattered. × 540.
Fig. 31. Oögonium after the formation of its basal wall, the protoplasm more withdrawn from the centre and the nuclei approaching in pairs. × 540.
Fig. 32. The nuclei larger, fewer, and fainter, and the vacuoles formed in the protoplasmic layer. × 800.
Fig. 33. The vacuoles have disappeared and the protoplasm is more contracted. × 800.
Fig. 34. The oöspores are formed, and the antheridia have produced fertilization-tubes which contain protoplasm and nuclei, but remain closed; *a* and *b,* two sections from the same oögonium. × 540.
Fig. 35. A fully developed oösphere with its single nucleus. × 800.
Fig. 36. Two oöspheres before the final nuclear fusions. × 800.
Figs. 37–39. *Saprolegnia monoica.*
Fig. 37. Sexual organs, mature. × 540.
Fig. 38. Both sexual organs from the same branch. × 540.
Fig. 39. An intercalary oögonium. × 200.
Figs. 40–42. *Saprolegnia mixta.*
Fig. 40. Two small oögonia, one with and one without an antheridium, the latter formed inside an empty sporangium. From Mississippi. × 200.
Fig. 41. An oögonium with antheridia. From Pennsylvania. × 200.
Fig. 42. An abnormally branched sporangium, not rare in this species. From Pennsylvania. × 74.
Figs. 43–45. *Saprolegnia ferax.* From Kentucky.
Fig. 43. An oögonium, on a branch growing through a sporangium. × 540.
Fig. 44. A cylindrical oögonium. × 540.
Fig. 45. Two oögonia on a forked branch. × 200.

Figs. 46–49. *Saprolegnia torulosa.*

Fig. 46. An oögonium with an antheridium, a rare case. × 200.

Fig. 47. Two cylindrical members of a series, the upper an oögonium, the lower a sporangium. × 200.

Fig. 48. Four members of a series, an oögonium, two sporangia, and the lowest still young. × 200.

Fig. 49. Two oögonia in series. × 200. The pits in the oögonial walls of this species are too inconspicuous to be brought out often with this power.

## *Plate XVII.*

Figs. 50–53. *Saprolegnia diclina.*

Fig. 50. The mouths of two sporangia appearing as if burst open by a force from within. ×200.

Fig. 51. An oögonium, with numerous antheridia. × 200.

Fig. 52. A similar oögonium on a very short branch, its pits few and small. × 540.

Fig. 53. An oögonium of the small form mentioned in the text. × 200.

Figs. 54, 55. *Saprolegnia asterophora.* From Cambridge, Mass.

Fig. 54. A two-spored oögonium with two antheridia; after a sketch by Prof. Trelease. × 850.

Fig. 55. A one-spored oögonium; from a slide by Prof. Trelease. × 540.

Figs. 56–59. *Saprolegnia Treleaseana.* From Wood's Holl, Mass.

Fig. 56. The only sporangium yet seen, with a zoöspore, *z*; after a sketch by Prof. Trelease. × 250.

Fig. 57. An hypha with two oögonia, one terminal, and one intercalary. × 74.

Fig. 58. A terminal oögonium, without antheridia. × 350.

Fig. 59. An intercalary oögonium, with antheridia. × 350.

Figs. 57–59, from a slide by Prof. Trelease.

Figs. 60–68. *Pythiopsis cymosa.*

Fig. 60. Two clavate sporangia, one young, *a*, and one empty, *b*. × 200.

Fig. 61. Two globular sporangia, one with its escape-papilla formed and with signs of spore-formation. × 200.

Fig. 62. Four sporangia arising by cymose branching of an hypha. × 350.

Fig. 63. Escape of zoöspores from a sporangium with several papillæ, only one of which has opened; *z*, three zoöspores killed soon after their escape; *z′*, two encysted zoöspores. × 350.

Fig. 64. A smooth-walled oögonium with a very short antheridial branch. × 540.

Fig. 65. An oögonium with two outgrowths of its wall; the antheridial branch longer than in 64. × 540.

Fig. 66. An oögonium with a single large outgrowth and an antheridial branch of diclinous origin. × 540.

Fig. 67. An oögonium with two ripe oöspores. × 540.

Fig. 68. A ripe oöspore showing its excentric structure, with several oil globules. × 940.

## *Plate XVIII.*

Figs. 69–73. *Achlya Americana.*

Fig. 69. A recently emptied sporangium, with the spore head. × 200.

Fig. 70. An hypha bearing numerous sexual organs. × 74.

Fig. 71. Details of oögonial and antheridial branches. × 350.

Fig. 72. A part of the ruptured wall of an oögonium, after treatment with chloroiodide of zinc, showing pits. × 540.

Fig. 73. Two ripe oöspores, showing their excentric structure. × 540.

Figs. 74–77. *Achlya megasperma.*

Fig. 74. Hypha bearing sporangia and oögonia. × 74.

Fig. 75. The end of an hypha, with oögonial and sterile antheridial branches. × 74.

Fig. 76. An oögonium with rather numerous antheridial filaments. × 200.

Fig. 77. An oögonium on a longer branch, with a single antheridium. × 200.

Figs. 78-81. *Achlya polyandra.*
Fig. 78. A sporangium with empty spore-membranes. × 200.
Fig. 79. An oögonium on a strongly recurved branch, showing the separation of oösphere origins, with two antheridial branches. × 200.
Fig. 80. A young oögonium, with much divided antheridial branches. × 200.
Fig. 81. Details of oögonium and antheridia. × 540.

## *Plate XIX.*

Figs. 82-86. *Achlya apiculata.*
Fig. 82. Two sporangia. × 200.
Fig. 83. A young oögonium with three antheridia. × 200.
Fig. 84. An unusually recurved oögonial branch. × 200.
Fig. 85. The more typical form of oögonial branch. × 200.
Fig. 86. Details of a small oögonium with two antheridia. × 540.
Figs. 87-89. *Achlya oblongata.*
Fig. 87. Hypha with sporangium and apical and lateral oögonia, antheridia omitted. × 74.
Fig. 88. Hypha with several racemosely arranged oögonia, tending to a pointed form. From Louisiana. × 74.
Fig. 89. An oögonium with several antheridial branches. × 200.
Figs. 90, 91. *Achlya oblongata*, var. *globosa.* From Alabama.
Fig. 90. An oögonium showing the oöspores grouped at one side. × 200.
Fig. 91. Details of sexual organs. × 200.
Figs. 92-95. *Achlya racemosa.*
Fig. 92. A sporangium. × 200.
Fig. 93. An oögonium with a single antheridium. × 200.
Fig. 94. Details of sexual organs of the commonest form, with two antheridia. × 540.
Fig. 95. Two oöspores, showing centric structure. × 540.
Figs. 96-98. *Achlya racemosa*, var. *stelligera.*
Fig. 96. A young oögonium, with three antheridia. × 200.
Fig. 97. An oögonium with a single very small antheridial branch. × 200.
Fig. 98. Details of sexual organs. × 540.

## *Plate XX.*

Figs. 99-102. *Achlya papillosa.*
Fig. 99. An hypha with a sporangium and an oögonium. × 200.
Fig. 100. A terminal and an intercalary oögonium, with antheridial branches. × 200.
Fig. 101. A strongly apiculate terminal oögonium. × 200.
Fig. 102. A terminal oögonium with a single antheridial branch. × 540.
Figs. 103, 104. *Achlya cornuta.*
Fig. 103. Three oögonia from the same hypha, one strongly apiculate. × 350.
Fig. 104. A three-spored apiculate oögonium. × 350.
Figs. 105-107. *Aphanomyces lævis.*
Fig. 105. Two oögonia from one hypha, with antheridia of diclinous origin. × 540.
Fig. 106. An oögonium thickly invested by antheridia. × 540.
Fig. 107. A young oögonium with antheridial branches of androgynous origin. × 540.
Figs. 108-111. *Aphanomyces scaber.*
Fig. 108. An oögonium of the rough form of the species, on a short, lateral branch. × 540.

Fig. 109. Two oögonia on the same hypha, the lower abortive, the upper with an antheridium. × 540.

Fig. 110. An oögonium of the smooth form of the species, with an antheridium. × 540.

Fig. 111. An old oögonium, with a ripe oöspore and no antheridium. × 540.

Figs. 112–114. *Dictyuchus Magnusii.* From Cambridge, Mass.

Fig. 112. An empty sporangium showing some of the openings for the exit of zoöspores; from a slide by Prof. Trelease. × 200.

Fig. 113. An oögonium with single oöspore and antheridial branch. × 500.

Fig. 114. A young oögonium with antheridial branch. × 500. The last two after sketches by Prof. Trelease.

Figs. 115–118. *Leptomitus lacteus.*

Fig. 115. An empty and a young sporangium, formed from successive segments of an hypha. × 200.

Fig. 116. The same, showing also the peculiar branching below a sporangium. × 200.

Fig. 117. Zoöspores encysted within a sporangium. × 200.

Fig. 118. Encysted and germinating zoöspores, and empty membranes pointing to diplanetism. × 540.

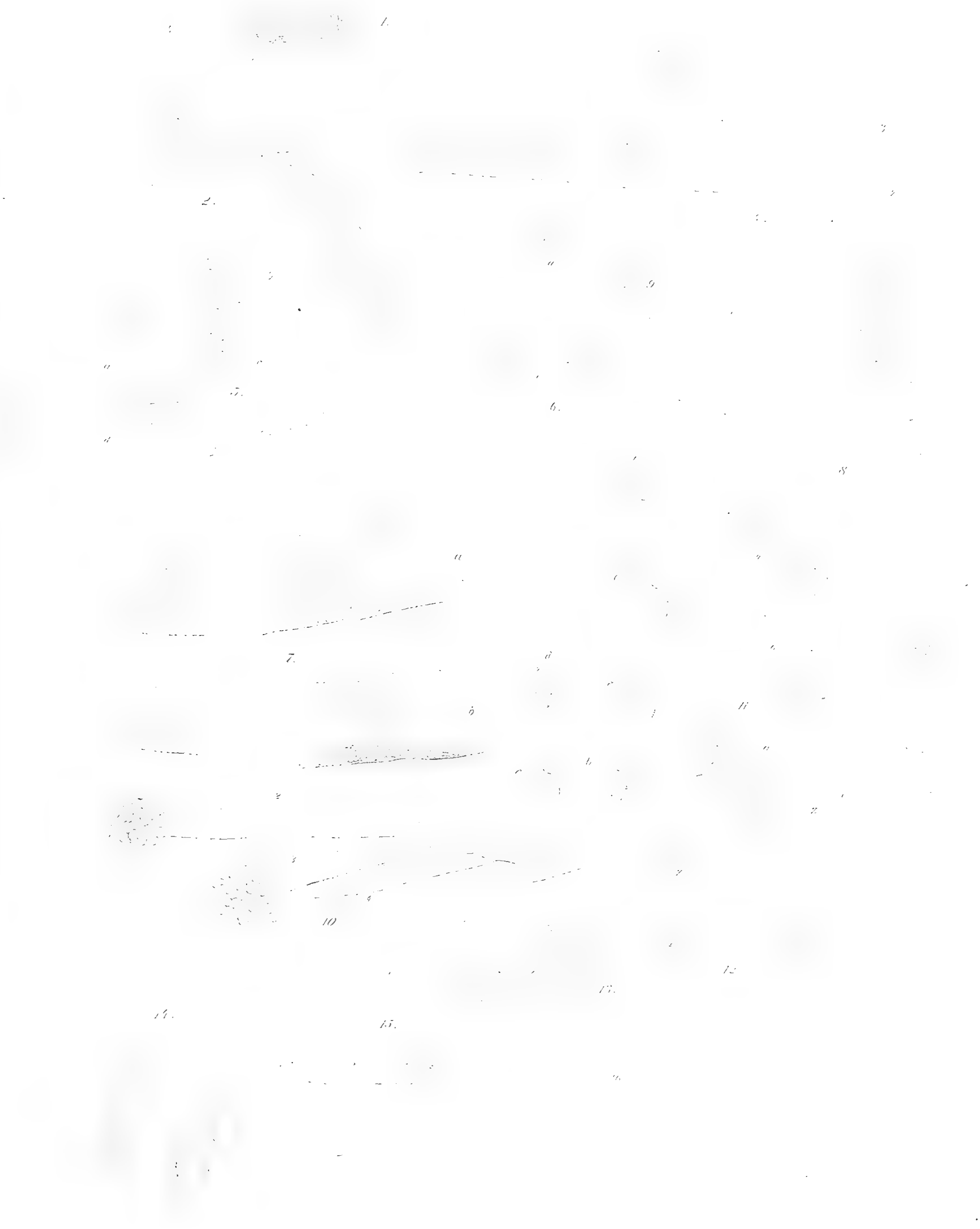
Figs. 119–121. *Apodachlya completa.* From Louisiana.

Fig. 119. Young sexual organs. × 540.

Fig. 120. Adult sexual organs, with ripe oöspores. × 540.

Fig. 121. Details of sexual organs, with peculiar structure in antheridial branches. × 940.

NOTE.—All drawings are from specimens obtained at Amherst, Mass., except where the contrary is noted.



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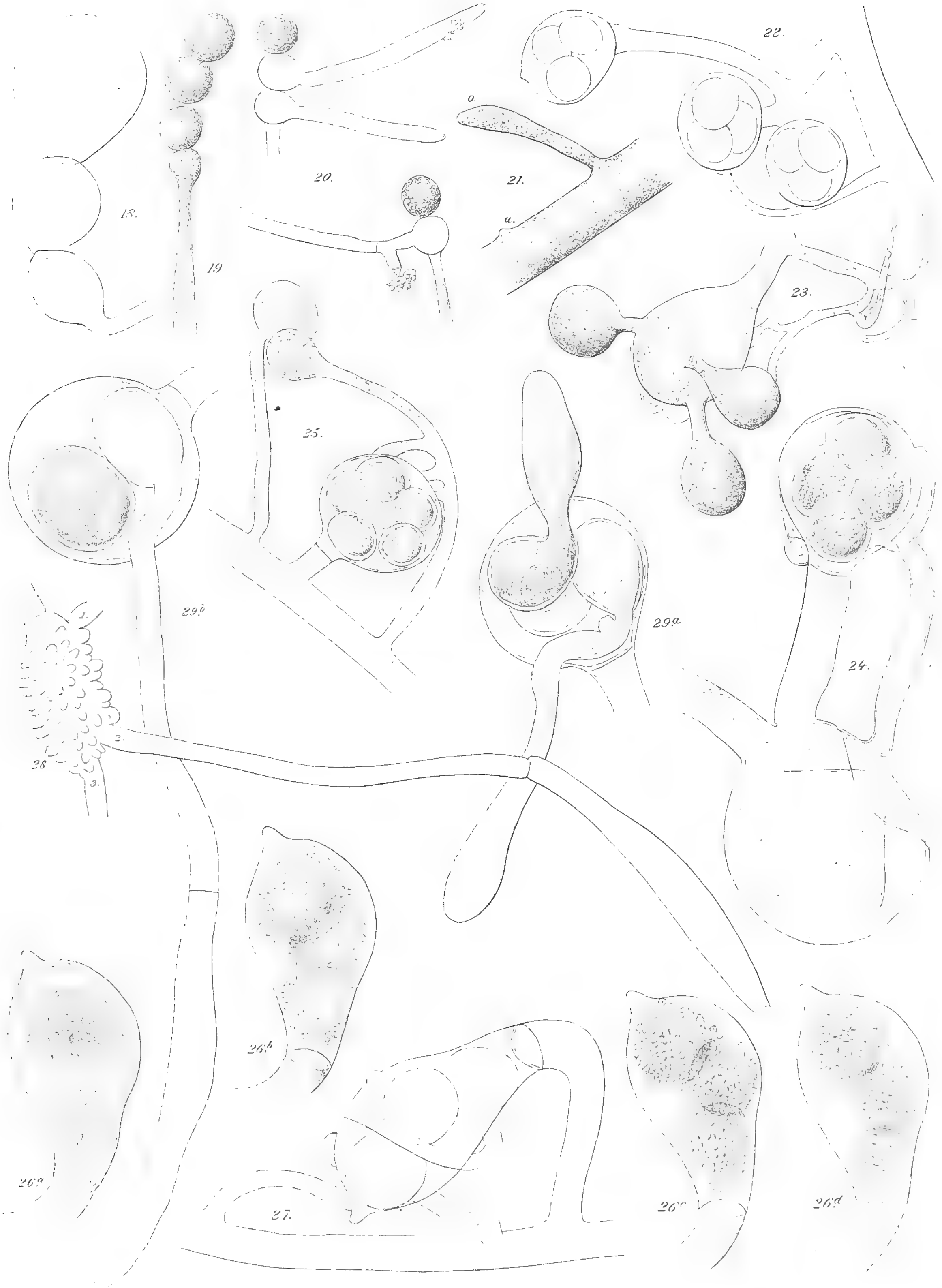

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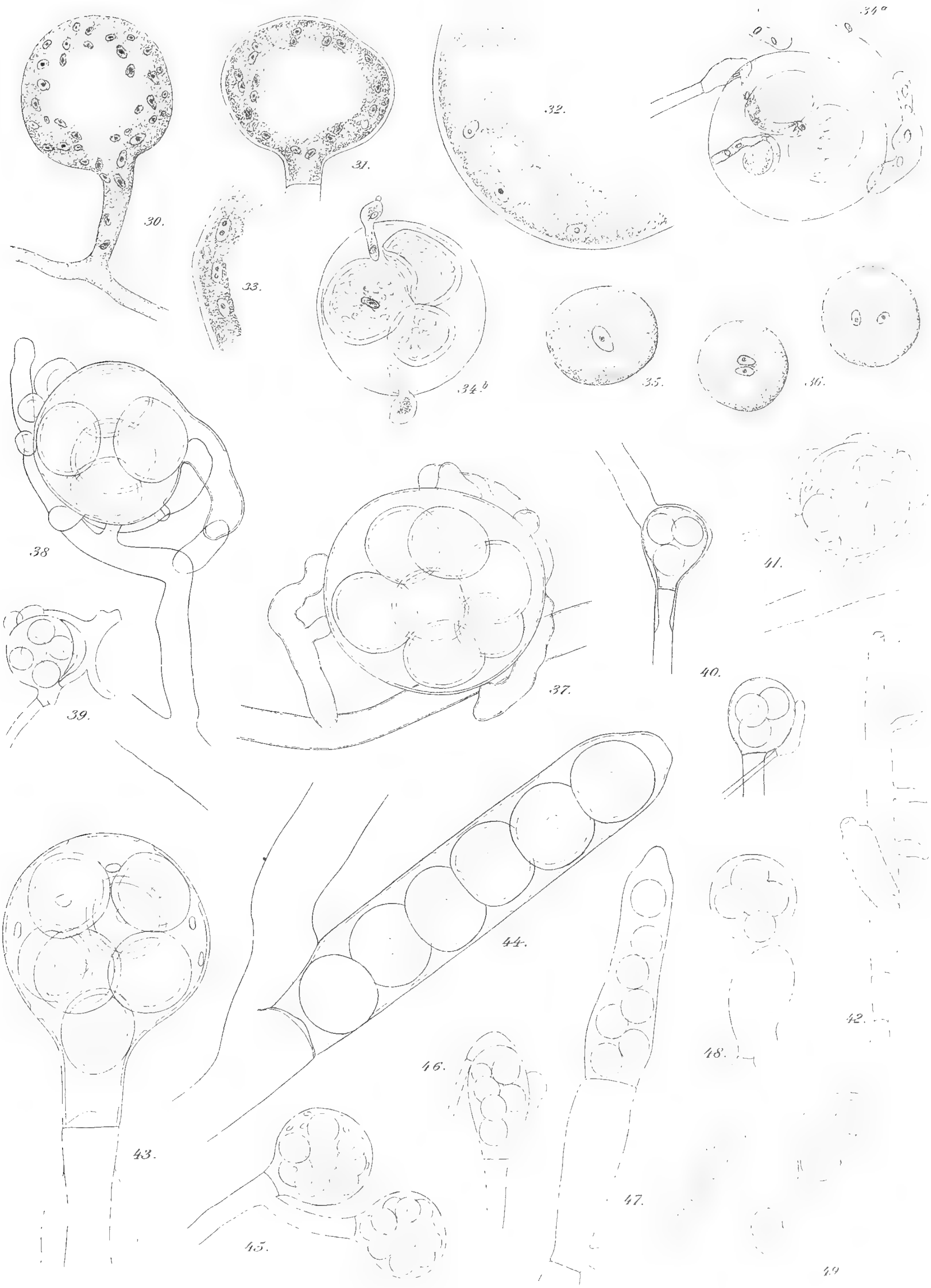
MORPHOLOGY OF SAPROLEGNIACEAE.



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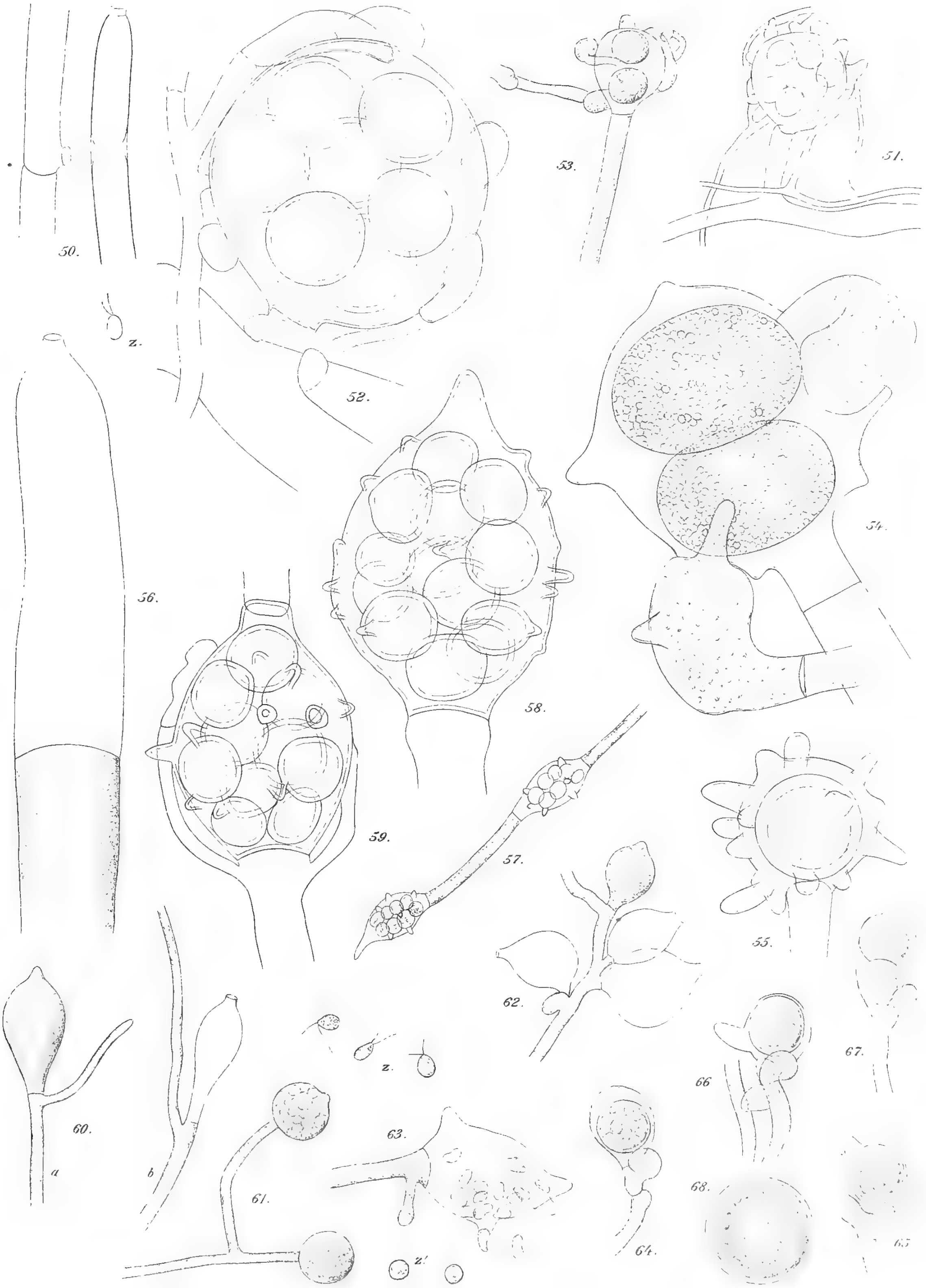
CYTOLOGY S. MONOICA, MIXTA, FERAX, TORULOSA.



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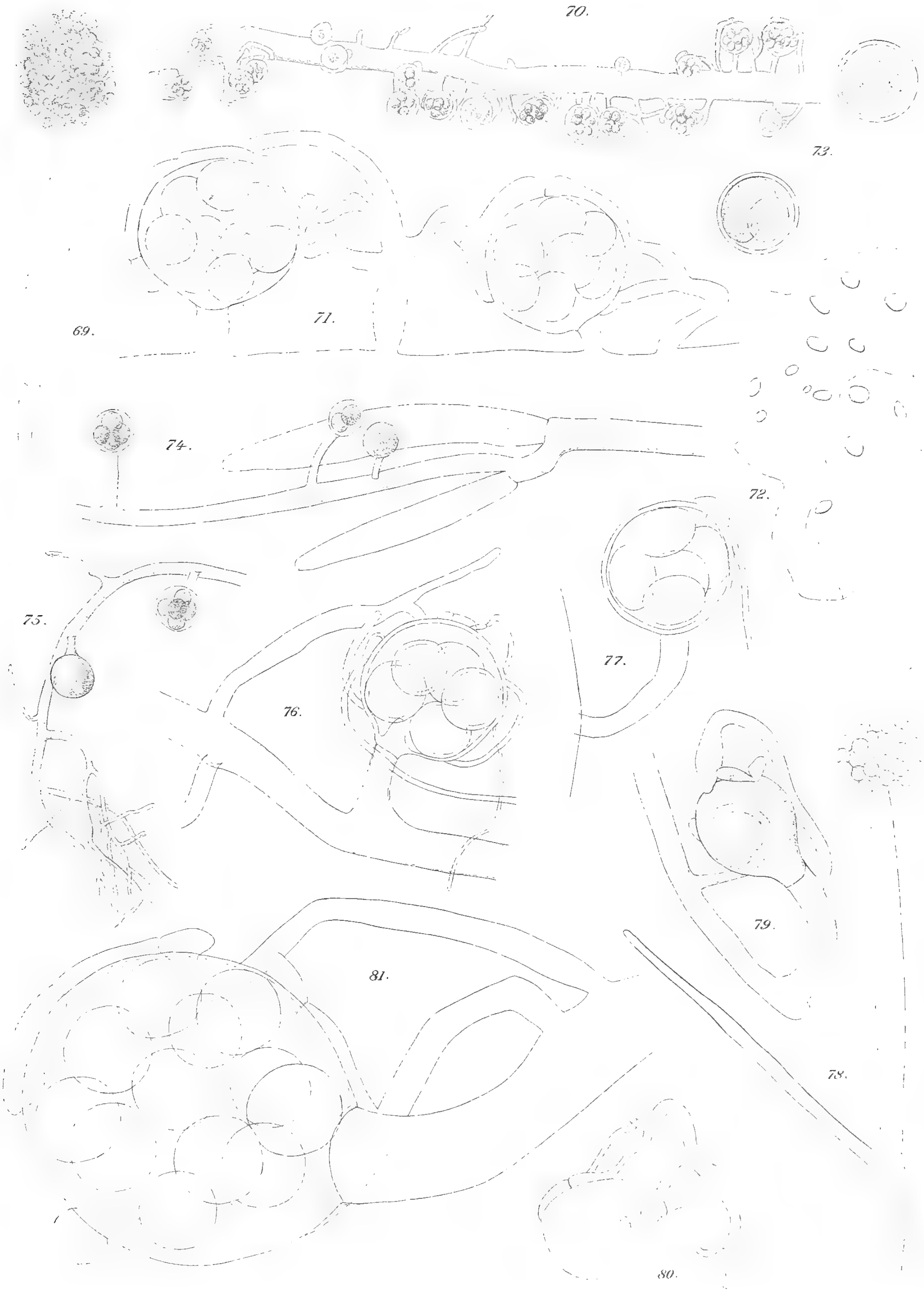
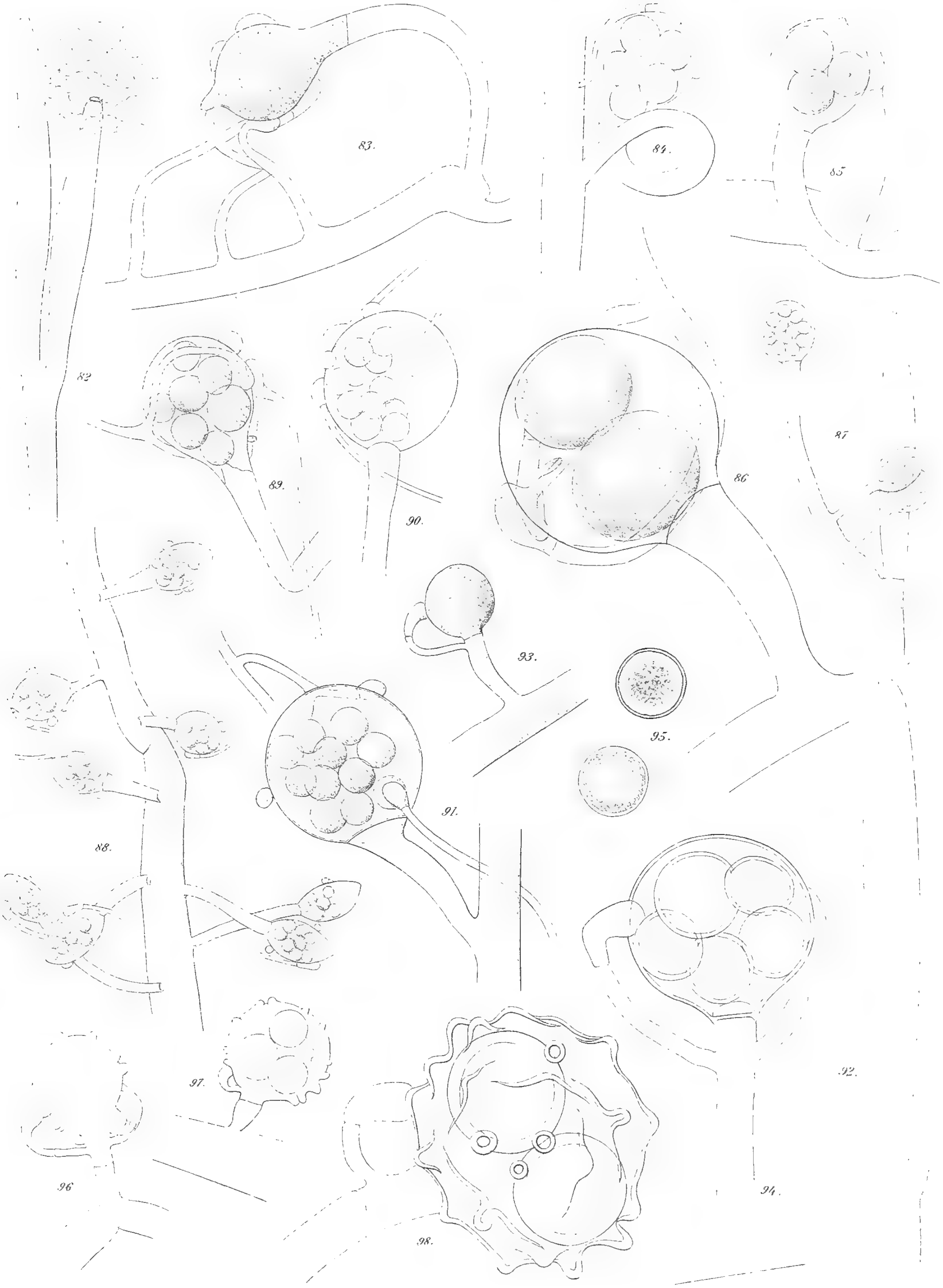
S DICLINA. ASTEROPHORA. TRELEASEANA. P. CYMOSA



J.E. Humphrey del. B. Meisel lith. Boston

A. AMERICANA, MEGASPERMA, POLYANDRA.



J.E. Humphrey del. F. Meisel lith. Boston

A. APICULATA, OBLONGATA, RACEMOSA.

J. E. Humphrey del.

F. Meisel lith. Boston

A. PAPILLOSA, CORNUTA. APH. LAEVIS, SCABER. D. MAGNUSII. L. LACTEUS. APOD. (?) COMPLETA.

# ARTICLE VI.

## RESEARCHES UPON THE CHEMICAL PROPERTIES OF GASES.

BY FRANCIS C. PHILLIPS, PH.D.

**Read before the American Philosophical Society, March 17, 1893.**

## CONTENTS.

## INTRODUCTION.

The purpose of the following research, as originally begun, was to study exhaustively the composition of natural gas as found in Western Pennsylvania. During a series of analyses by Bunsen's methods, using eudiometers calibrated with great care, and making readings by means of a Grunot cathetometer of superior construction, many difficulties were encountered which were not easily overcome. More exact methods for the positive identification of the various constituents of a gas mixture seemed necessary, and finally a study of the qualitative reactions of gases was undertaken. Since the publication of Bunsen's Gasometrische Methoden, the introduction of the various forms of apparatus proposed by Hempel and Winkler has tended to greatly simplify quantitative gas analysis.

The majority of absorption gasometric methods are based upon the assumption that the contraction undergone by the volume of a gas on exposure to a liquid reagent is not only a measure of the percentage of a particular constituent of the gas mixture, but that the identity of such constituent is established by the same operation. This assumption is very often warranted by the facts, but occasionally leads to error. Qualitative methods, for the recognition of different gases, have usually been held wholly subordinate to quantitative absorption or explosion methods. Quantitative analyses are far more reliable if the constituents to be determined can be positively identified by independent methods; and it is somewhat strange that, heretofore, the qualitative side of gas analysis should have received so small a share of attention. In the following work, an attempt has been made to collect together the more important reactions of the commonly occurring gases. The results must be regarded as a first attempt only, inasmuch as improved methods of preparation and purification will doubtless involve the necessity of corrections in certain cases. Accurate methods of qualitative gas analysis are likely to prove of increasing importance in the study of the atmosphere, in the laboratory and in the chemical arts. The following subdivision of the subject has been found convenient:

1. Phenomena of oxidation of hydrogen and hydrocarbons by air in presence of finely divided metals and other oxidizing agents.

2. Reactions of gases towards various metallic salts and other compounds used in solution, and in a dry state at high temperatures.

## I. OXIDATION TEMPERATURES.

**Preparation of Palladium Asbestos.**—Long-fibred asbestos, washed by hydrochloric acid, dried and weighed, was moistened with palladium chloride solution. Alcohol was dropped on the asbestos and ignited. After burning off the alcohol a few times, the asbestos was heated in a Bunsen burner flame, and the treatment with palladium chloride and alcohol repeated. With care, it is possible to obtain a fairly uniform coating of palladium, although the metal tends somewhat to collect on the surface of the fibres. Asbestos fibre, containing an amount of palladium equal to 6 per cent. of the total asbestos plus palladium, was used in the following experiments:

About 0.3 gm. of this asbestos was placed in a glass tube of one-eighth-inch bore. This tube was then heated in an iron oven, having its lower portion filled up to the level of the glass tube with iron turnings, so that the glass tube rested on and was partly covered by the turnings. A thermometer was inserted into the turnings. In some of the experiments the apparatus described on p. 154 was used. In the *Berichte der d. chem. Ges.*, 1879, pp. 636 and 1006, two articles appeared by W. Hempel on the determination of hydrogen in gas mixtures by means of palladium sponge. In the former article it is proposed to remove the hydrogen by occlusion: in the latter, by oxidation. Winkler, in his Technical Gas Analysis (p. 81), employs palladium asbestos for oxidation and determination of hydrogen in presence of methane (and other paraffins), in water gas, coal gas, etc. In order to study the limits and possibilities of these methods, and their applicability to various gas mixtures, the following experiments were made:

1. **Hydrogen.**—Hydrogen is not easily obtained pure; all authors who have had occasion to study its properties agree upon this. The purest zinc contains carbon, and hydrogen made by the action of sulphuric acid upon this metal is contaminated by traces of hydrocarbons. Other metals have been tried. Aluminium was dissolved in sulphuric acid and also in caustic soda solution; magnesium and cadmium were dissolved in hydrochloric acid; sodium and potassium in water. In every case, however, the hydrogen evolved contains hydrocarbons, as was shown by the production of carbon dioxide on burning. After various trials, the following plan has been found to give satisfactory results: The purest zinc obtainable (such as is sold in sticks for use in Marsh's test for arsenic) was dissolved in dilute sulphuric acid. The gas was passed (1) through a 6 per cent. solution of permanganate of

potassium acidulated by sulphuric acid; (2) through a glass tube containing cotton coated with precipitated oxide of copper; (3) through alkaline permanganate; (4) the gas was kept in contact with bromine water for twenty-four hours; (5) well washed by soda solution (for the action of copper oxide as a purifying agent for hydrogen, see Lionet, *Fresenius Zeitschrift*, 1880, p. 344). I have found precipitated carbonate of copper in moist condition to answer better than the oxide, especially for removing sulphuretted hydrogen. Hydrogen so purified contained only traces of a paraffin which, calculated as $CH_4$, amounted to less than 0.02 per cent. of the hydrogen. By very careful tests no phosphorus, arsenic, sulphur or antimony could be found.

*Expt.* 1.—A mixture was made of hydrogen and air in the following proportions:

| | |
|---|---|
| Air | 80 |
| Hydrogen | 20 |

This mixture, contained in a gas-holder, was caused to flow slowly over 6 per cent. palladium asbestos, which was contained in an one-eighth-inch glass tube heated in the oven. The rate of flow of the hydrogen and air mixture could be controlled by causing it to bubble through sulphuric acid before entering the palladium asbestos tube. Some anhydrous copper sulphate was placed in the far end of the palladium tube, which by its change of color to a bright blue serves as a delicate moisture indicator.

| TEMPERATURE OF ASBESTOS TUBE. | RATE OF GAS FLOW. | RESULT. |
|---|---|---|
| 20° | 100 cub. cent. in five min. | No moisture. |
| 30° | " " " " " " | " " |
| 40° | " " " " " " | " " |
| 50° | " " " " " " | Moisture formed. |
| 20° | " " " " " " | No moisture. |
| 30° | " " " " " " | " " |
| 40° | " " " " " " | " " |
| 50° | " " " " " " | " " |
| 55° | " " " " " " | Moisture formed. |

Hence, absolutely dry hydrogen is not easily burnt by palladium asbestos below a temperature of 50°-60°.

At the above rate (100 c.c. in five minutes), there is a strong tendency to cause glowing of the palladium asbestos, not throughout, but in minute points where the palladium had accumulated in thicker particles. This glowing may take place while the tube is at any temperature between 15° and 100°, and depends wholly on the rate of flow of the hydrogen mixture. It is independent of the temperature outside the tube, and it is therefore not possible to prevent or arrest it except by reducing the rate of flow. The hydrogen by its rate of burning determines the temperature, and the low specific heat of the palladium and feeble conductivity of the asbestos necessarily increase the tendency to glow. Using air and hydrogen (5 : 1) repeatedly, no explosion ever occurred, although the palladium often glowed with great intensity. This is also true of palladium asbestos containing 30 per cent. of palladium, and when the temperature was carried to 135° C. Air containing only 1 per cent. of hydrogen may cause intense glowing of the palladium if the rate of flow is rapid. Immersion of the tube in cold water will not prevent glowing. Caution is necessary, should a mixture of oxygen and hydrogen be exposed to palladium. In experiments made with tubes of one-millimeter bore, and at a temperature of 100°, it was found that the hydrogen in burning causes a series of sharp explosions, very different from the quiet and slow oxidation which invariably characterizes the mixture of air and hydrogen.

*Expt.* 2.—To determine the degree of completeness of the oxidation of hydrogen by palladium asbestos.

| | |
|---|---|
| Air | 90 |
| Hydrogen | 10 |

The palladium tube was heated to 60°–70° C. Gas escaping from the palladium tube was passed through oil of vitriol and phosphoric anhydride, in order to dry thoroughly; then through a second (porcelain) tube containing palladium asbestos; and finally into a small weighed tube of phosphoric anhydride. The second palladium tube was heated to intense redness. It was found that absolutely no moisture was formed in the second contact with palladium, although 5 liters of the gas mixture were used and the rate of flow varied from 40 to 100 bubbles per minute. It was shown, moreover, that complete oxidation is independent of the glowing of the palladium.

Hence the oxidation of hydrogen by air in presence of palladium is complete at a temperature of 60°–70° when the gas mixture is dry. Quantitative experiments, to be detailed later, showed that in the case of air containing 0.2 of hydrogen a correct determination of the hydrogen was possible. The temperature in this case was 100° C. If the hydrogen and air mixture is moist, oxidation is easily and completely attained at ordinary temperatures.

Hydrogen is said to ignite at a temperature of 552° C. (Le Chatelier, *Bull. Soc. Chim.*, 1883, p. 2).

*Expt.* 3. *Gold Asbestos.—*

| | |
|---|---|
| Air | 90 |
| Hydrogen | 10 |

No change occurred till the gold asbestos was strongly heated over flame, and even then the oxidation was exceedingly slow, so that repeated passages of the gas were required to produce complete oxidation. In the preceding experiment a Hempel's apparatus was used.

*Expt.* 4. *Platinum Asbestos.*—

| | |
|---|---|
| Air | 90 |
| Hydrogen | 10 |

The results were scarcely distinguishable from those obtained with palladium asbestos. Palladium causes oxidation with somewhat greater intensity and at lower temperatures. Determinations of hydrogen in mixtures of known proportions, using a Hempel apparatus, gave very correct results.

*Expt.* 5. *Iridium Asbestos.*—

| | |
|---|---|
| Air | 90 |
| Hydrogen | 10 |

When used in a Hempel apparatus in the cold or at 100° C., iridium seemed to have very little influence, causing only a slight contraction in volume, even after the gas had passed the iridium many times.

*Expt.* 6.—

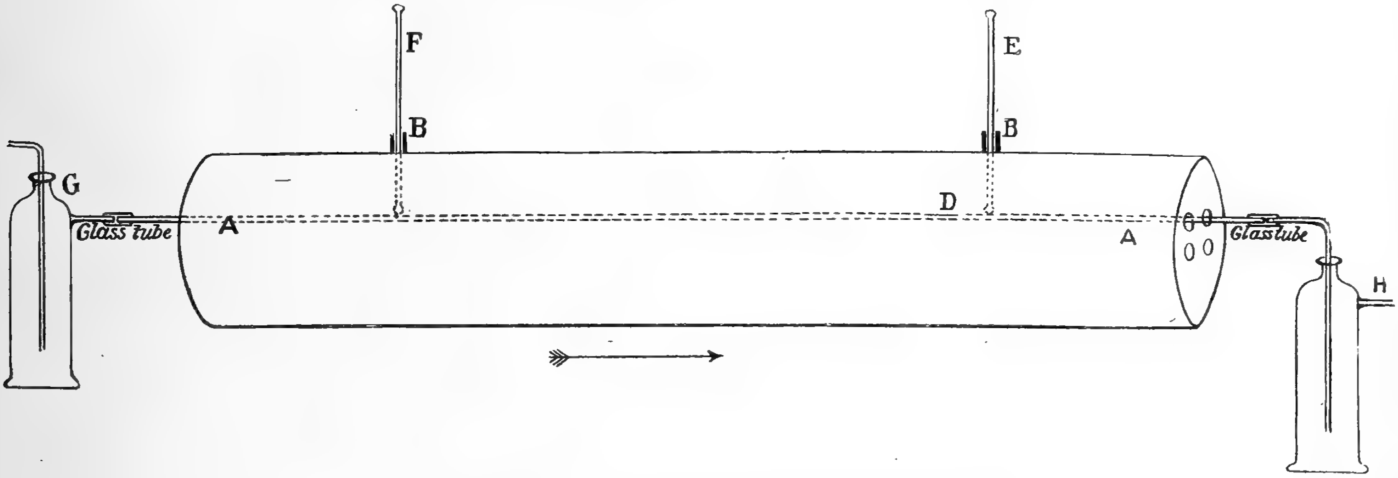
| | |
|---|---|
| Air | 90 |
| Hydrogen | 10 |

Palladium asbestos was moistened with a solution of carbonate of potash and dried at a heat which was insufficient to cause fusion or sintering. In several trials the alkali was found to seriously retard oxidation of the hydrogen, which was not fully burnt until the gas mixture had been repeatedly (in one case ten times) passed through the tube at 100°.

## HYDROCARBONS.

*Description of Apparatus.*—A, is an iron gas pipe, six inches in diameter and thirty-four inches long, closed at both ends by heavy asbestos board. Four iron pipes of three-sixteenths-inch bore are placed in the centre, passing through the asbestos ends, and giving the apparatus the appearance of a boiler with four flues.

B, B, are two side necks of one-half-inch pipe. The whole interior space around the four small iron pipes is filled with iron turnings. Glass tubes of one-eighth-inch bore, containing the metal-coated asbestos or other reagent, could be pushed through the small iron pipes. Thermometers were placed in the side necks B, B. Supposing the arrow to represent the direction of flow of the gas current through the gas tubes, the metal-coated asbestos was, in the experiments, placed at the point D, and of the two thermometers E was kept a few degrees higher than F, the purpose being to have the gas heated nearly to the temperature of the hottest part of the oven before it reached that point. Thus it was not possible for the gas stream to exert a cooling effect upon the metal-coated asbestos. This apparatus is superior to an ordinary sheet-iron oven, as the glass tubes are heated by actual contact rather than by radiation. Repeated trials have shown that if a thermometer be inserted in the side neck, and a second one in one of the long, horizontal iron tubes, the difference in the indications of the two thermometers will amount only to an insignificant fraction of a degree Centigrade. Nitrogen-filled mercury thermometers were used up to 300° in the following experiments, and in order to measure higher temperatures, metallic salts of known fusing point were employed. A few grains or crystals of the carefully purified salt were placed in a fine glass tube previously drawn out to a point. Such a tube was placed in the side neck of the iron oven and plunged into the iron turnings. The temperature of oxidation of the hydrocarbon gas could then be ascertained to occur between the melting points of two salts. This method, which is simply an adaptation of the process commonly used for the determination of melting points, proved very satisfactory. It was not possible to employ an air thermometer, as this would have necessitated an inconveniently large oven. The following list of substances, with their melting points, includes those which were used in the experiments detailed below.



Iron oven used in experiments upon oxidation temperatures.

| | |
|---|---|
| Potassium nitrate | 339° |
| Potassium chlorate | 359° |
| Lead iodide | 383° |
| Cadmium iodide | 404° |
| Barium chlorate | 414° |

| | |
|---|---|
| Thallium iodide | 439° |
| Lead chloride | 498° |
| Silver bromide | 527° |
| Potassium iodate | 582° |
| Barium nitrate | 593° |

(Landolt and Bornstein's Tables and *J. Ch. Soc.*, 1888, p. 63.)

The following general method was used in studying oxidation temperatures of hydrocarbons:

Air containing a small measured percentage of the hydrocarbon was agitated with caustic soda solution to remove carbon dioxide. It was then caused to flow through the bottle (G) containing lime water. This served to show whether the gas had been completely freed from $CO_2$. The gas then traversed the palladium asbestos, or other reagent contained in the glass tube in the oven, and finally a second bottle of lime water (H). On heating the oven, the temperature of oxidation of the hydrocarbon could be recognized by the precipitate of carbonate of lime in the second lime water bottle. As an indicator for $CO_2$ in the oxidation experiments, solutions of baryta strontia and lime were all tried. The solubilities of the carbonates, according to Fresenius, are as follows:

| | | | | | |
|---|---|---|---|---|---|
| $BaCO_3$ | one part | in | 14,137 | parts | water. |
| $SrCO_3$ | " | " | " 18,045 | " | " |
| $CaCO_3$ | " | " | " 10,601 | " | " |

Baryta water appears to be the most delicate test. On account of its extreme sensitiveness, however, it is not easily preserved free from turbidity, and lime water was found sufficiently sensitive for almost all purposes. The same general method above detailed was used in all the following experiments.

It seemed desirable at the outset to test the question, Do the hydrogen and carbon of a hydrocarbon burn simultaneously?

In the oxidation of a hydrocarbon in presence of excess of air, it seems probable that the hydrogen and carbon must burn simultaneously to $H_2O$ and $CO_2$. It is possible, however, that under the conditions above described a selective oxidation of hydrogen might occur, involving the formation of a condensation product.

Thus $CH_4$ might yield acetylene:
$2\,CH_4 + O_3 = 3\,H_2O + C_2H_2$ and no $CO_2$.
$2\,CH_4$ might yield $C_2H_4$;
$2\,CH_4 + 2\,O = C_2H_4 + 2\,H_2O$ and no $CO_2$.

As reagents for the detection of moisture in a gas, the following substances were tried:

Anhydrous cobalt chloride, anhydrous copper sulphate, phosphoric anhydride, a mixture of green vitriol with ferricyanide of potassium, the green vitriol being in its crystallized form and containing therefore 7 mols. water. This salt and the ferricyanide of potassium were ground separately and mixed just previously to the experiment (anhydrous sulphate of iron was found not to give satisfactory results). A little of the mixture placed in the end of the glass tube was found to be a delicate indicator for moisture, assuming quickly a deep blue color.

*Expt.* 7.—

| | |
|---|---|
| Air | 96.9 |
| Ethylene | 3.1 |

This gas mixture was passed through soda solution and then dried by oil of vitriol. It then traversed the palladium asbestos, which was gradually heated in the oven. At the far end of the same glass tube the gas passed over about 0.1 gm. of the green vitriol and ferricyanide of potassium mixture (cold), and finally into lime water. It was found that the lime water became milky a few moments before the powder turned blue. This change to blue took place, however, immediately afterwards and before any further increase in the temperature of the oven had occurred. As the lime water is a much more sensitive reagent towards $CO_2$ than is the green vitriol mixture towards moisture, it is natural that the $CO_2$ should produce its effect a little in advance of the water vapor. Similar experiments were tried with methane. The results were the same as with ethylene.

*Expt.* 8.—

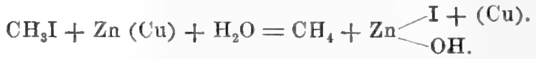
| | |
|---|---|
| Air | 96.9 |
| Methane | 3.1 |

This mixture (moist) was found, after passing the palladium asbestos, to cause no reduction in palladium chloride solution (see reactions in solution), and hence no oxidation of $CH_4$ to $C_2H_4$ had occurred. There is therefore no reason to suppose that, under the circumstances which prevailed in the apparatus above described, either constituent of the hydrocarbon is oxidized before the other. The hydrocarbon yields directly $CO_2$ and $H_2O$.

## PARAFFINS.

2. METHANE.—This hydrocarbon was prepared by the method of Gladstone and Tribe (*Jour. Chem. Soc.*, 1884, p. 1541). Methyl iodide of normal boiling point was caused to flow in admixture with alcohol upon "copper-zinc couple." The resulting gas was freed from alcohol vapor by oil of vitriol. It was then washed with bromine water, and the bromine vapors subsequently removed by ferrous sulphate solution. Finally it was passed over dry palladium chloride at 50°, to remove any possible

traces of hydrogen. The following explanation of the reaction is given by the authors cited:



$$CH_3I + Zn\ (Cu) + H_2O = CH_4 + Zn\begin{cases} I + (Cu). \\ OH. \end{cases}$$

200 c.c. of the methane so prepared were burned, and the products aspirated through soda solution. On testing the latter for halogen, no traces could be found. From this it was evident that no vapor of methyl iodide had escaped decomposition by the zinc. Methane is obtained when chloroform dissolved in alcohol is dropped upon zinc powder.

$$CH_3Cl + 3\ H_2O + 6\ Zn = 3\ ZnO + 3\ ZnCl_2 + 2\ CH_4$$

(Sabanejeff, *Ber.*, IX, p. 1810). This method was found to give very satisfactory results. The process usually given in the text-books, by heating acetate of soda with alkali, is very unsatisfactory both as regards purity and quantity of product.

*Expt.* 9. *Palladium Asbestos.*—

| | |
|---|---|
| Methane | 3.1 |
| Air | 96.9 |

Oxidation to $CO_2$ occurred at the following temperatures:

(1) Above melting point of $CdI_2$ (404°).
(2) " " " " $CdI_2$ (404°).
(3) " " " " $Ba(ClO_3)_2$ (414°).
(4) " " " " $CdI_2$.
(5) " " " " $Ba(ClO_3)_2$ (414°).

In the above trials methane from methyl iodide was used.

The preceding experiment was repeated, using methane from chloroform. In six different trials the temperature of oxidation was found to be between the melting points of $CdI_2$ and AgCl (404° to 451°). In one trial, oxidation occurred considerably above the melting point of AgCl.

The temperature of oxidation of methane is therefore extremely high as compared with that of hydrogen.

Hempel, in his excellent work on gas analysis, says that methane prepared from sodium acetate is oxidized by palladium at 210°. My results do not confirm this statement. The difference is possibly due to impurities in the methane.

*Expt.* 10. *Palladium-Platinum Asbestos.*—

| | |
|---|---|
| Air | 96.9 |
| Methane | 3.1 |

Asbestos was moistened alternately with palladium chloride and platinum chloride and the metals reduced by burning alcohol, as already described, the object being to produce an intimate mixture of both in finely divided state. Oxidation occurred in four trials between the melting points of $CdI_2$ and AgCl.

The mixture of the two metals is, therefore, no more efficient than palladium alone.

*Expt.* 11. *Platinum Asbestos.*—

| | |
|---|---|
| Air | 96.9 |
| Methane | 3.1 |

Oxidation occurred in five trials at a temperature just below the melting point of AgCl.

*Expt.* 12. *Gold Asbestos.*—

| | |
|---|---|
| Air | 96.9 |
| Methane | 3.1 |

Oxidation occurred at a temperature of dull redness. In this last experiment a Hempel apparatus was used.

According to Mallard and Le Chatelier, methane inflames at 780° (*Ann. des Mines*, 1880, p. 201).

3. ETHANE.—This gas was prepared from ethyl iodide by the method of Gladstone and Tribe already described. The resulting gas was purified from alcohol vapors by prolonged contact with oil of vitriol. It was then treated with potash solution and with palladium chloride (dry). 200 c.c. of the gas so purified yielded, on burning, no trace of halogen when the product of combustion was aspirated through potash solution.

*Expt.* 13. *Palladium Asbestos.*—

| | |
|---|---|
| Ethane | 3.1 |
| Air | 96.1 |

In several trials made with ethane, the temperature of oxidation was found to be between the melting points of cadmium iodide and silver bromide. Parallel trials were then made, using air containing 3.1 per cent. of methane (from methyl iodide) in one tube and 3.1 per cent. ethane in the other. Both tubes were charged with portions of the same lot of palladium asbestos, and both were heated simultaneously in the iron oven, so that the conditions to which the two gases were subjected were as nearly as possible identical. In ten trials oxidation occurred in both tubes in the neighborhood of the melting point of silver chloride; but it was noticeable that the methane was oxidized in eight of the experiments a little earlier (and hence at a slightly lower temperature) than the ethane. The more complex hydrocarbon $C_2H_6$ is at least as stable, and probably somewhat more stable, than the lower $CH_4$. A parallel case is probably to be found in the difference in stability of the corresponding alcohols towards reducing agents. Methyl alcohol is decomposed on warming with powdered zinc, with formation of CO and H, while ethyl alcohol is unaltered except at a red heat (Jahn, *Grundsätze der Thermochemie*, p. 150).

4. PROPANE.—This hydrocarbon was prepared by Gladstone and Tribe's method, from isopropyl iodide and "copper-zinc couple." The reaction is much slower than in the case of methane and ethane; the yield is, however, satisfactory. The same method of purification was used as in the case of methane. The gas was found to be free from iodine compounds.

*Expt.* 14. *Palladium Asbestos.*—

| | |
|---|---|
| Propane | 3.1 |
| Air | 96.9 |

Oxidation occurred at the following temperatures:

(1) Above melting point of potassium nitrate (339°).
(2) Just below melting point of potassium nitrate (339°).
(3) " above " " " " " (339°).
(4) Just below melting point of lead iodide (383°).
(5) At melting point of potassium chlorate (359°).
(6) " " " " " " (359°).

5. ISOBUTANE.—This hydrocarbon was prepared by the method of Gladstone and Tribe from isobutyl iodide and "copper-zinc couple." It was purified by the method followed in the case of the preceding hydrocarbon, and was proved to be free from iodine compounds.

*Expt.* 15. *Palladium Asbestos.*—

| | |
|---|---|
| Isobutane | 3.1 |
| Air | 96.9 |

Oxidation occurred at the following temperatures:

(1) At 236°
(2) " 225°
(3) At 250°
(4) " 220°
(5) At 225°
(6) " 250°

*Expt.* 16.—The same mixture of air and isobutane was conducted over ruthenium asbestos (prepared by the use of ruthenium chloride in the same manner as the palladium asbestos already described). Oxidation occurred at the following temperatures:

(1) At 250°
(2) " 236°
(3) At 230°
(4) " 225°
(5) At 222°
(6) " 214°

As regards this more easily oxidizable hydrocarbon ruthenium and palladium have almost the same action.

6. PENTANE.—Petroleum gasolene, which had been kept several weeks in contact with concentrated sulphuric acid, was fractionated and the fraction, boiling at

about 37° C., was used for the following experiments. It was mainly pentane, as was shown by a vapor density determination, but contained, no doubt, small quantities of other low-boiling paraffins. Purified air was aspirated through a Woulfe bottle containing a little of the liquid.

*Expt.* 17. *Palladium Asbestos.*—Oxidation occurred:

(1) At 210°
(2) " 200°
(3) At 180°
(4) " 170°
(5) At 210°

7. HEPTANE.—"Theoline," a commercial product formerly replacing benzol in the San Francisco market, and manufactured by distilling a resin from the tree *Pinus sabiniana*, was shown by Thorpe (*Chem. Soc. Jour.*, 1879, p. 296) to consist of normal heptane in an impure state. By digestion with oil of vitriol the paraffin is obtained pure and of constant boiling point (between 98° and 99° C.). Heptane was the highest paraffin used in the trials of oxidation temperatures. As this hydrocarbon is readily obtained in a state of purity, and as it was the most complex paraffin employed, it seemed desirable to ascertain whether, on oxidation by palladium asbestos, any unsaturated hydrocarbon resulted.

*Expt.* 18. *Palladium Asbestos.*—Air was aspirated through a Woulfe bottle containing heptane and then through the heated palladium asbestos tube. Oxidation occurred at the following temperatures:

(1) At 270°
(2) " 270°
(3) At 280°
(4) " 275°
(5) At 300°
(6) " 290°

While the experiment was in progress, the air escaping from the palladium asbestos tube was passed through soda solution to absorb the $CO_2$ formed, and then into palladium chloride solution and finally into lime water. The palladium chloride was reduced to metal and the lime water following it was rendered milky (see reactions of CO in solution). This result occurred only when the air was insufficient for complete oxidation of the heptane. With an excess of air, only $CO_2$ and $H_2O$ were formed, and no unsaturated hydrocarbon could be detected (olefines and acetylenes would have caused a reaction in palladium chloride solution; see reactions of these hydrocarbons in solution). It seems, therefore, that oxidation of the paraffins $CH_4$, $C_2H_6$ . . . . . . . . $C_7H_{16}$ (even when carried on at the lowest possible temperatures) by excess of air in presence of palladium asbestos yields only $CO_2$ and $H_2O$, although by no means in quantities proportional to the amount of the hydrocarbon originally used.

## OLEFINES.

8. ETHYLENE.—This hydrocarbon, on account of the ease with which it is prepared and its low temperature of oxidation, is well suited to the study of reactions,

and it has received in the present work a larger share of attention than any other gas.

Ethylene was prepared by the method of Erlenmeyer and Bunte (*Ann. der Chem. u. Pharm.*, Vol. CLXVIII, p. 64). The yield is, however, small as compared with the theoretical. The older method of Mitscherlich (Kolbe, *Lehrb. d. Organ. Chem.*, Vol. I, p. 349), according to which the vapor of boiling alcohol is led into a mixture of 10 parts sulphuric acid and 3 parts water, at a temperature of 165° C., yields more ether than ethylene, although it possesses the advantage that frothing is avoided. Whatever the strength of the sulphuric acid used, there is always produced a large proportion of ether which cannot be absorbed by rapid bubbling through sulphuric acid. Part of this ether vapor is removable by agitation with a large volume of cold water. Its complete removal requires prolonged contact with oil of vitriol. The gas was purified by soda solution containing bichromate of potash and digested with oil of vitriol for several days.

Ethylene was also prepared by the action of zinc upon $C_2H_4Br_2$ (*J. Ch. Soc.* (2), XII). Ethylene dibromide dissolved in 2 parts alcohol was introduced by tap funnel into a flask containing zinc powder, and connected by a reversed condenser with a gasometer. The same method of purification by sulphuric acid was used as in the preceding case. This method is in every way very satisfactory for the preparation of small quantities of ethylene.

*Expt.* 19. *Palladium Asbestos.*—

| | |
|---|---|
| Ethylene | 3.1 |
| Air | 96.9 |

Oxidation occurred:

(1) At 210°
(2) " 180°
(3) " 224°
(4) At 200°
(5) " 220°
(6) " 191°
(7) At 224°

The ethylene burns therefore more easily than either methane or ethane.

*Expt.* 20. *Palladium-Platinum Asbestos.*—The same mixture of ethylene and air was used. The range of temperatures at which oxidation occurred was about the same as in the case of the preceding experiment, showing that the mixture of the two metals is no more efficient than palladium alone.

*Expt.* 21.—

| | |
|---|---|
| Air | 96.9 |
| Ethylene | 3.1 |

30 per cent. palladium asbestos was moistened with cobalt nitrate solution, dried and ignited in order to coat the asbestos with peroxide of cobalt. On passing the gas mixture, carbon dioxide was produced at the following temperatures:

(1) At 277°
(2) At 250°
(3) At 260°

Hence, the presence of an easily reducible metallic oxide does not seem to increase the oxidizing action of the palladium.

*Expt.* 22.—Several trials were then made in order to ascertain whether by the same general method ethylene could be exhaustively burned. It was found that, using air containing 3.1 per cent. of ethylene, oxidation is only complete (*i. e.*, to $CO_2$ and $H_2O$) when the palladium asbestos is brought to a temperature of bright redness. At a dull red heat the hydrocarbon may pass partially unburnt. A platinum wire spiral (heated by an electric current) was found to be less efficient than palladium asbestos.

*Expt.* 23. *Absorption of Ethylene by Palladium.*—Pure ethylene (*i. e.*, unmixed with air) was passed over 2 gms. of finely divided palladium contained in a Hempel tube heated to 100. A considerable absorption of the gas occurred, varying in several trials from ½ to 5 c.c., according to the duration of the experiment. Unmixed with an excess of air it appears, therefore, that ethylene may undergo an absorption which might cause serious errors in a quantitative gas analysis. With palladium asbestos (6 per cent. palladium) no occlusion of ethylene sufficient to effect the volume of the gas could be observed.

*Expt.* 24. *Ruthenium Asbestos.*—

| | |
|---|---|
| Air | 96.9 |
| Ethylene | 3.1 |

Oxidation occurred at the following temperatures:

(1) At 294°
(2) " 281°
(3) At 274°
(4) " 320°

*Expt.* 25. *Osmium Asbestos.*—

| | |
|---|---|
| Ethylene | 3.1 |
| Air | 96.9 |

Owing to the volatility of osmium in the form of oxide, some difficulty was found in preparing osmium asbestos. Osmic acid was reduced by alcohol and the reduced metal spread upon asbestos. Oxidation occurred at the following temperatures:

(1) At 150°
(2) " 140°
(3) " 135°
(4) " 120°
(5) At 116°
(6) " 160°
(7) " 170°
(8) " 160°
(9) At 160°
(10) " 135°

In the preceding experiments it has been shown that oxidation of the hydrocarbon does not occur each time at the same temperature. The variations are often so great as to preclude the supposition that a cause is to be sought in different conditions of the experiment. To ascertain as fully as possible the limits of variation in the temperature of oxidation, the following trials were made:

*Expt.* 26.—Instead of metal-coated asbestos, a platinum wire one millimeter thick and one inch long was placed in the one-eighth-inch glass tube in the oven. The same mixture of air and ethylene was used as in the preceding experiments. As in all previous work, the oven was allowed to cool down after each trial and before the next one was begun. In every case the temperature was very gradually raised until oxidation, as indicated by the precipitation in the lime water, occurred. The gas stream was carefully regulated, being maintained at a uniform rate in all the trials. Oxidation occurred at the following temperatures:

(1) At 270°
(2) “ 290°
(3) “ 390°
(4) “ 290°
(5) “ 310°
(6) “ 289°
(7) “ 295°
(8) “ 300°
(9) At 300°
(10) “ 265°
(11) “ 210°
(12) “ 217°
(13) “ 220°
(14) “ 225°
(15) “ 200°
(16) “ 210°
(17) At 220°
(18) “ 255°
(19) “ 210°
(20) “ 220°
(21) “ 235°
(22) “ 200°
(23) “ 210°
(24) “ 225°

As no effort had been spared to secure absolute uniformity of conditions, the conclusion seems justified that oxidation of the hydrocarbon ethylene occurs within somewhat wide limits of temperature.

*Expt.* 27.—Air containing 3.1 per cent. ethylene was passed through a glass tube containing pieces of glass tubing which had been previously ignited. No oxidation occurred at the melting point of bromide of silver (427°) during four hours.

*Expt.* 28.—

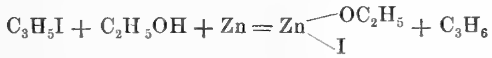
| | |
|---|---|
| Air | 96.9 |
| Ethylene | 3.1 |

This mixture was passed, as before, over a platinum wire and the temperature gradually raised until a carbon dioxide reaction was produced. This occurred at 240°. The gas stream was then continued while the temperature was allowed to fall. The lime water was repeatedly replaced, but each time became rapidly milky. Oxidation was continuous until the temperature fell to about 110°, at which point fresh lime water was found to remain clear. Hence, platinum having been sufficiently heated to induce oxidation of ethylene by atmospheric oxygen, retains this power while the temperature is lowered to a point which would have been wholly insufficient to cause such oxidation if the temperature were rising instead of falling. This is true, moreover, when the gas stream flows at the rate of 20 to 50 bubbles per minute; so slowly, therefore, that there is no possibility that this effect is attributable to an actual burning of the gas with flame. Similar results were obtained in trials with palladium asbestos and ruthenium asbestos, and also when methane and ethane were used.

9. **Propylene.**—This gas was prepared by the action of potash on propyl iodide (Erlenmeyer, *Zeitschr. f. Chem.*, 1864, p. 647). 80 gm. of propyl iodide were heated with 50 gm. of potash and 50 gm. of alcohol over the water bath. The following reaction occurs:

$$C_3H_7I + KOH = KI + H_2O + C_3H_6.$$

The flask containing the potash and alcohol being connected with a reversed condenser and gently warmed, the propyl iodide is slowly added by a tap funnel, and at a temperature of 40° the reaction begins. The gas so produced was washed with water and digested with oil of vitriol (cold), in which it is insoluble, and finally washed by potash solution. Propylene was also prepared from allyl iodide (Gladstone and Tribe, *J. Ch. Soc.*, 1874, and also Niderist, *Ann. Ch. Pharm.*, CXCVI, p. 358). 20 c.c. of allyl iodide mixed with three volumes of alcohol were poured over 30 gm. powdered zinc containing 10 gm. of mossy zinc heated in a flask over a water bath. Powdered zinc becomes during the reaction a hard, compact mass. The addition of mossy zinc and constant agitation serve to facilitate the process. The reaction is as follows:



$$C_3H_5I + C_2H_5OH + Zn = Zn\begin{array}{l} -OC_2H_5 \\ \diagdown I \end{array} + C_3H_6$$

The propylene so prepared was purified as in the preceding method. Careful tests demonstrated the absence of iodine compounds from the product. Beilstein and Wiegand (*Ber.*, 1882, p. 1498) prepare propylene by the action of propyl alcohol upon phosphoric anhydride. In employing this method, 120 gm. $P_2O_5$ were placed in a flask provided with a reversed condenser and propyl alcohol gradually added by a tap funnel. The action is at first very violent and requires cooling of the flask; becomes less and less intense, and finally it is found necessary to heat the flask over asbestos. After about 130 c.c. of propyl alcohol had been added the reaction ceased. The method is satisfactory although the yield is small. A method proposed by Klaus and Kerstein (*Ber.*, Vol. IX, p. 695), according to which zinc dust is heated with glycerine, was tried, but with unsatisfactory results. The intense frothing of the mixture renders the process uncontrollable. In the various trials, propylene, as prepared by the first three methods just described, was used. That prepared from allyl iodide seemed to be the purest, as judged by the reactions in solution to be detailed later.

In the oxidation experiments below cited, propylene from allyl iodide is understood to have been used.

*Expt.* 29. *Palladium Asbestos.*—

| | |
|---|---|
| Propylene | 3.1 |
| Air | 96.9 |

Oxidation occurred:

(1) At 170°
(2) " 180°
(3) At 200°
(4) " 200°

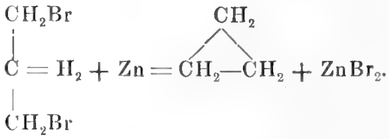
*Expt.* 30. *Ruthenium Asbestos.*—The same mixture of propylene and air was used. Oxidation occurred:

(1) At 235°
(2) " 252°
(3) At 256°
(4) " 239°

*Expt.* 31. *Rhodium Asbestos.*—The same mixture of air and propylene. Oxidation occurred:

(1) At 283°
(2) " 284°
(3) At 270°
(4) " 290°

10. TRIMETHYLENE.—This very interesting hydrocarbon was obtained from trimethylene dibromide by the action of metallic zinc (Gustavson, *Ber.*, 1887, p. 707, R). 20 c.c. trimethylene dibromide with 60 c.c. of alcohol were poured over 60 gm. of zinc dust. The reaction is as follows:



The trimethylene dibromide molecule, on losing bromine, assumes the form of a ring and the resulting hydrocarbon is therefore a saturated compound. The gas is evolved at a gentle heat (the temperature should not exceed 60°), and is purified by passing through a condenser cooled by ice, by digestion with sulphuric acid and finally by dilute permanganate of potash solution. It has been shown by Wagner (*Ber.*, 1888, p. 1230) that trimethylene prepared by the above reaction is liable to contain propylene, which may be removed by prolonged contact with a weak solution of permanganate of potash (which converts propylene into its corresponding glycol but does not attack the trimethylene).

*Expt.* 32. *Palladium Asbestos.*—

| | |
|---|---|
| Trimethylene | 3.1 |
| Air | 96.9 |

Oxidation occurred:

(1) At 260°
(2) At 290°
(3) At 270°

*Expt.* 33. *Osmium Asbestos.*—The same mixture of air and trimethylene. Oxidation occurred:

(1) At 200°
(2) " 200°
(3) At 180°
(4) " 165°

This hydrocarbon seems to stand intermediate between propane and propylene as regards resistance to oxidation.

11. Isobutylene.—This hydrocarbon was prepared by the action of sulphuric acid upon isobutyl alcohol, by the method of Puchot (*Ber.*, 1883, p. 2284, R). 100 gm. isobutyl alcohol were mixed (cold) with 100 gm. oil of vitriol, 160 gm. sulphate of lime and 40 gm. bisulphate of potash. This mixture was heated, using a flask with reversed condenser, to a temperature sufficient to cause a rapid evolution of gas. Besides butyl ether and other less volatile compounds, impurities in vapor form occur in the isobutylene resulting from this process, which is on this account unsatisfactory. The yield is comparatively large.

By the action of potash upon isobutyl iodide a much purer product is obtained. Isobutyl bromide may be used instead of the iodide. In either case the use of potash in powdered form greatly facilitates the reaction. Potassium iodide, being more soluble in alcohol than potassium bromide, the alkyl iodide is to be preferred in reactions of the above type, as potassium bromide, resulting from the use of alkyl bromides, encrusts the potash and retards the reaction.

Isobutylene prepared by the latter method was used in the following experiments. It was carefully purified by digestion (cold) with sulphuric acid, and on testing was found to be free from iodine compounds. Isobutylene is soluble in water to a considerable extent and should therefore be collected over salt solution.

*Expt.* 34. *Palladium Asbestos.*—

| | |
|---|---|
| Isobutylene | 3.1 |
| Air | 96.9 |

Oxidation occurred:

(1) At 180°
(2) " 160°
(3) At 170°
(4) " 185°
(5) At 155°

12. Acetylene.—100 gm. crushed potash were placed in a flask connected with reversed condenser. A mixture of 50 gm. ethylene bromide with 150 gm. alcohol was added in small portions by a tap funnel. The escaping acetylene was caused to bubble through boiling potash solution and then absorbed by ammoniacal cuprous chloride solution. The resulting red precipitate was washed with ammoniacal copper solution, then by weak ammonia. After washing, the precipitate was brought into a flask and decomposed by hydrochloric acid, and the acetylene thus

evolved was collected. The copper precipitate consists of $Cu_2C_2$, and on treatment with hydrochloric acid undergoes the reaction:

$$Cu_2C_2 + 2\ HCl = Cu_2Cl_2 + C_2H_2.$$

(For an interesting description of this compound, see Keyser, *Am. Chem. Jr.*, 1892, p. 285.)

The precipitate of copper acetylide must be preserved in an unoxidized state previous to its treatment with hydrochloric acid in order to liberate acetylene. If exposed to air during washing, the precipitate is found to remain almost unacted upon by hydrochloric acid, and the yield of acetylene from the copper compound will be insignificant. On this account the washing should be conducted in an atmosphere of carbon dioxide.

A very interesting method for the preparation of acetylene by the action of water upon barium carbide has been described by Maquenne (*Compt. Rend.*, CXV, p. 558). Barium carbonate is reduced by magnesium powder in presence of excess of carbon. As the result of the somewhat violent reaction barium carbide is formed. On moistening with water this carbide is decomposed, yielding nearly pure acetylene.

*Expt.* 35. *Palladium Asbestos.*—

| | |
|---|---|
| Acetylene | 3.1 |
| Air | 96.9 |

Oxidation occurred:

(1) Above melting point of potassium nitrate (339°).
(2) " " " " potassium chlorate (359°).
(3) " " " " potassium nitrate (339°).
(4) " " " " " " (339°).

It was found by careful tests that no CO is formed in the case of the above mixture. In fact, no other products resulted than $CO_2$ and $H_2O$.

Acetylene seems therefore to be more stable towards heated air in presence of palladium asbestos than the olefines, and in this respect even to rival the paraffins.

13. BENZOL.—The low boiling point of benzol and the common occurrence of its vapor in gas mixtures justify its consideration in connection with the gaseous hydrocarbons.

*Expt.* 36.—Air aspirated through benzol (prepared from benzoic acid) and then through palladium asbestos was found to yield carbon dioxide at the following temperatures:

(1) At 290° (2) At 250° (3) At 270°

Benzol vapor causes the palladium to glow very easily; in fact, much more readily than any of the hydrocarbons heretofore tried.

14. Alcohol Vapor.—*Expt.* 37.—Employing the same method detailed in the case of benzol, oxidation was found to occur:

(1) At 160°
(2) " 240°
(3) At 150°
(4) " 150°

15. Xylols.—Very careful experiments with the vapors of meta-, para- and ortho-xylol were tried, as it seemed possible that these three isomers might exhibit different temperatures of oxidation dependent upon the position of the side chain. No satisfactory results were obtained, however, on account of the want of constancy of these hydrocarbons as regards oxidation temperature.

16. Carbonic Oxide.—This gas was prepared by the action of sulphuric acid upon oxalic acid. It was purified by caustic soda solution.

*Expt.* 38. *Palladium Asbestos.*—

| | |
|---|---|
| CO | 10 |
| Air | 90 |

Oxidation occurred at the following temperatures:

(1) At the melting point of potassium nitrate (339°).
(2) " " " " " " " (339°).
(3) (290°).
(4) At the melting point of potassium nitrate.
(5) Above the melting point of potassium nitrate.
(6) At the melting point of potassium chlorate (359°).

Trials were also made in varying the rate of flow, and also with different proportions of carbonic oxide and air. The results did not differ materially from those just cited. This gas seems to stand intermediate between methane and ethylene in its resistance to oxidation.

*Expt.* 39. *Ruthenium Asbestos.*—Using the same air mixture, oxidation occurred at the following temperatures:

(1) At 194°
(2) " 209°
(3) At 182°
(4) " 188°

The preceding experiments serve to illustrate some important facts regarding the oxidation of gaseous hydrocarbons.

1. The temperature of oxidation is mainly dependent upon the solid bodies with which the gas is in contact—a fact which is not new.

2. Two phases are often, but not always, to be observed in the process of oxidation. As the temperature rises, a point is reached at which a minute and scarcely recognizable trace of carbon dioxide appears. After the slow oxidation has continued for some time and gradually increased during a rise of temperature of 20, 30,

or even more degrees, a sudden intense reaction occurs in the lime water, suggesting the change from smouldering fire to actual flame. Very often this slow oxidation is not observed and the carbon dioxide reaction occurs in the lime water suddenly and with full intensity. The hydrocarbon molecule seems to exist at high temperatures in a condition of unstable equilibrium towards oxygen. In the preceding statements the temperatures given are those of decided and intense reaction in the lime water.

3. The oxidation of a hydrocarbon by air, under conditions similar in all respects, does not occur always at the same temperature. It may vary within rather wide limits of the thermometer scale. A variation in the proportion of hydrocarbon and air does not seem to materially influence the oxidation temperature.

4. The paraffins are the most stable towards heated air in presence of palladium. Acetylene and carbonic oxide stand next in order. The olefines are the most easily oxidized.

5. Of the members of the same homologous series of hydrocarbons, the lower are the more stable towards oxidizing influences.

6. Hydrogen stands alone among combustible gases in undergoing oxidation under the influence of palladium-coated asbestos in the cold.

7. Oxidation of gaseous hydrocarbon in excess of air involves the simultaneous formation of $CO_2$ and $H_2O$.

8. In all cases where air is in excess, oxidation is complete (*i. e.*, yielding only $CO_2$ and $H_2O$), even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, $CO_2$ may be partly replaced by CO among the products of oxidation.

9. As regards oxidizing power, the metals which I have studied might be arranged in the following order, beginning with the most active: (1) Osmium, (2) palladium, (3) platinum, ruthenium, (4) iridum, (5) rhodium, (6) gold.

Osmium is decidedly the most powerful, causing oxidation of ethylene even below 150°. Rhodium is less efficient as regards oxidation of hydrogen than palladium. Oxidizing power is apparently not dependent upon atomic weight. Of these metals, osmium in fine division is the most easily converted into an oxide. Heated in a flame it burns, exhibiting much the appearance of burning lamp-black, and yields, as is well known, the volatile osmium tetroxide. At much lower temperatures the metal is slowly oxidized and volatilized. Palladium in fine division is converted into a stable oxide, $Pd_2O$, on heating to redness (Wilm, *Ber.*, 1892, p. 220). Platinum and gold are not oxidizable in air at any temperature. Ruthenium oxidizes to a sesquioxide at a red heat. Rhodium is convertible into a monoxide. In the case of the majority of these metals, the tendency to form an unstable oxide, which readily gives up its oxygen, explains the oxidizing power upon hydrocarbons. When it is considered however that platinum, which induces oxidation nearly as readily as palladium, does not produce directly an oxide when heated in air, the oxidizing power possessed in common by these metals seems to require further explanation.

10. At a bright red heat and in excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper.

11. Glowing of the palladium is by no means essential to slow oxidation where a mere carbon dioxide reaction for the recognition of the hydrocarbon gas or vapor is to be attained (that is, when a quantitative combustion is not aimed at).

12. The proportion of finely divided metal used upon asbestos seems to be immaterial. Palladium asbestos containing 2 per cent. of palladium is nearly as efficient as that containing 30 per cent. As it is difficult to distribute the metal uniformly on the asbestos fibre, the higher percentage, by collecting irregularly, is more liable to cause glowing. Berliner (*Ann. Phys. Chem.*, n. F., 35, p. 791) states that the catalytic action of each metal, in the case of the reaction

$$H_2 + O = H_2O,$$

begins at a fixed temperature and increases with rise of temperature. The oxidation temperature for platinum foil is about 270°; for copper, 280°; for zinc, 350°; while aluminium has no action at 440°. At constant temperatures the quantity of water formed is constant. My experiments do not confirm these statements.

Krause and Meyer (*Ber.*, 1891, p. 698, R) state that in the presence of mercury hydrogen begins to oxidize at 305°, while increasing temperature accelerates the oxidation. In contact with glass alone, hydrogen burns between the limits 650° and 730°.

## MIXTURES OF HYDROGEN WITH AIR AND HYDROCARBONS.

A great number of experiments have been undertaken to ascertain the influence of hydrogen upon the oxidation of hydrocarbons in presence of metals. Of these the following is a summary: In a mixture of methane and air, a small proportion of hydrogen does not influence the oxidation of the methane provided the rate of flow of the gas mixture over the palladium asbestos is very slow. Water will form readily, but no carbon dioxide, unless the temperature rises to about the melting point of cadmium iodide (400°), that is to say, the temperature at which the methane would be oxidized if no hydrogen were present. If the gas mixture flows rapidly, the burning hydrogen may so intensely heat the palladium as to cause it to glow. This involves an immediate production of carbon dioxide. With a slow movement of the gas, considerable volumes of hydrogen may be burned without formation of a trace of carbon dioxide. This is the conclusion reached by Hempel; but I have found the temperature at which the hydrocarbon is oxidized to be much higher than he supposes (about 200°). The same statement is true of hydrogen and ethane, and in general it may be said that the paraffins in presence of hydrogen and excess of air only undergo oxidation by palladium asbestos when the too rapid oxidation of the hydrogen causes glowing of the palladium.

The same general phenomena are observed in the case of mixtures of olefines and hydrogen with air. The temperatures of oxidation of the olefines are always lower than those of the corresponding paraffins. Below the temperature needed for oxidation a contraction in volume often occurs, due probably to occlusion by palladium. The addition of hydrogen to a mixture of air and carbon monoxide lowers the temperature of oxidation of the carbon monoxide by palladium asbestos. While the carbon monoxide alone in air was oxidized at temperatures above 300°, in presence of hydrogen it may yield $CO_2$ below 100°.

As has already been stated, the slow oxidation by palladium of a hydrocarbon in excess of air involves the conversion of carbon into carbon dioxide only, no carbon monoxide being produced. Experiments were made with a gaseous mixture having the following composition:

| | |
|---|---|
| Propane | 3.1 |
| Hydrogen | 2. |
| Air | 94.9 |

Oxidation of the paraffin occurred at temperatures varying from 270° to the melting point of potassium nitrate (339°), but in no case was any carbon monoxide produced nor could any olefines be detected in the gas after passing the palladium.

## ACTION OF HYDROCARBONS UPON METALLIC OXIDES.

As the temperature of oxidation by air in presence of finely divided metals seemed to vary within rather wide limits, it was possible that the differences might be due to a lack of absolutely uniform conditions in the various trials. So much care had been taken as regards the temperature and preparation of metal-coated asbestos that there was no positive ground for supposing that the apparatus and materials employed were in any way at fault.

To still further study the matter, a series of trials was made of the temperature of reaction between reducing gases and the following compounds: Oxide of copper, chromate of lead, oxide of silver, permanganate of silver, bichromate of silver. Only a few of the results need be cited here. Silver bichromate heated in ethylene yielded carbon dioxide at the following temperatures:

(1) At 320°
(2) " 279°
(3) " 300°
(4) At 250°
(5) " 265°
(7) " 260°
(8) At 280°

In each trial fresh silver bichromate was used. The results are, therefore, similar to those obtained with palladium asbestos. Barely visible traces of carbon dioxide were usually shown by the lime water in advance of the strong reaction which occurred later. As in the case of oxidation by palladium in air, the hydrocarbon appears to undergo a kind of "smouldering" which changes rather suddenly as the temperature rises to a condition of much more intense oxidation.

Hempel has suggested that it might be possible, by a process of selective oxidation, to remove consecutively the various constituents of a mixture of combustible gases and in this way establish a method of analysis. The similarity in the properties of the various gases whose oxidation temperatures I have studied, towards air and in presence of metals as well as towards silver bichromate, seems to render doubtful the possibility of such a method. From this statement is to be excepted the determination of hydrogen, the methods for which have been so highly perfected by Hempel and Winkler.

## II. QUALITATIVE REACTIONS OF GASES.

The recognition of any gas in a complex mixture is still a matter of difficulty in many cases, although in a few instances methods of identification are coming to be well known. Serious difficulties oppose all attempts at a system of qualitative analysis of gas mixtures. There are but few groups of gases (if the name "group" be understood to include all gases chemically alike); moreover, the members of a group exhibit much closer relationships than are to be found among the metals of any one of the groups of Fresenius. The following classification of gases has been found convenient for purposes of study:

Group 1. Hydrogen.
Group 2. Carbon monoxide.
Group 3. Methane, ethane, propane, the butanes, etc.
Group 4. Ethylene, propylene, trimethylene, the butylènes, etc.
Group 5. Acetylene, allylene, etc.
Group 6. Sulphur compounds: Hydrogen sulphide, methyl hydrosulphide ($(CH_3)SH$), methyl sulphide ($(CH_3)_2S$), carbon oxysulphide ($COS$), carbon bisulphide.
Group 7. Carbon dioxide.
Unclassified: Nitrogen, oxygen.

In a study of the kind proposed, it is of importance to take into account not only gases that are permanent under ordinary conditions but also vapors of liquids which are liable to occur in small quantities, such as carbon bisulphide, benzol, several of the lower paraffins and olefines, etc.

### METHODS EMPLOYED.

In the case of reactions between gases and solid substances, the solid to be tried was placed in a glass tube of one-eighth-inch diameter, which could then be heated to any given temperature in the iron oven previously described, while the gas was caused to stream through the tube. In the case of reactions in solution, two methods were used.

1. The gas was caused to flow through a capillary tube into the solution contained in a test-glass. The escaping gas could then be led into a second and, if necessary, a third test-glass in order to ascertain the action of the solution used in the first test-glass.

2. The gas was collected in glass-stoppered bottles over water, a small quantity of a solution introduced by means of a tap funnel with the lower end of its stem bent upward, then the bottle closed and kept inverted at any given temperature for sufficient length of time (usually from a few months to several days) to ascertain if a reaction had occurred. The former method answers well for gases which are easily controlled in a slow continuous stream and obtainable in large quantity. The latter method is more economical as regards the gas to be used, and is better suited to gases where some slight but difficultly removable impurity is suspected to occur of a character liable to effect the reagent (such as the traces of hydrocarbons present in hydrogen made from zinc and sulphuric acid). In such cases the smaller the volume of gas to be used in a trial the better. A reaction may usually be obtained with from 20 to 50 c.c. of gas. Small bottles having well-ground, flat-topped glass stoppers answer well, as they may be kept standing inverted and may, if heat is to be applied, be placed inverted in boiling water. It is hardly necessary to add that, when inverted, such bottles may be used to hold gas in contact with a reagent for long periods without danger of loss.

### HYDROGEN.

Hydrogen for the following experiments was prepared and purified as already described (p. 151). Reactions were tried in bottles and by causing the gas to bubble through the solutions, as just detailed.

### 1. *Reactions in Solution.*

| REAGENT. | REACTIONS. |
|---|---|
| Palladium chloride | The solution is slowly but completely reduced, cold or at 100°. The precipitated palladium usually collects as a black powder. Sometimes it is deposited as a film on the glass. |
| Platinum chloride* | Very slow but complete reduction, cold or at 100°. The reduced metal appears as a black powder. |
| Gold chloride | Unchanged. |
| Silver nitrate | Unchanged if the fluid contains a trace of free nitric acid. |
| Ammoniacal silver nitrate | Slowly reduced, the silver appearing as a black powder |
| Iridium chloride | Unchanged. |
| Rhodium chloride | Unchanged. |
| Potassium rutheniate | Slowly reduced. The orange color of the fluid disappears and metallic ruthenium is precipitated as a black powder. |
| Cerium dioxide dissolved in dilute sulphuric acid | Unchanged. |
| Potassium permanganate,† neutral | Extremely slow reduction, the purple color changing to brown. |

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* Mendeleeff, *Principles of Chemistry*, Vol. II, p. 353.

† Meyer and Askenasy (*Ber.*, 1882, p. 410, R) find that electrolytic hydrogen reduces potassium permanganate.

| | |
|---|---|
| Permanganate, acidulated with sulphuric acid | Bleached slowly. |
| Permanganate, alkaline | Slowly changes to brown. |
| Potassium bichromate, acidulated with sulphuric acid | Unchanged, cold or at 100°. |
| Mercuric chloride | Unchanged. |
| Osmic acid | Unchanged. Prolonged contact in bright light yields traces of reduction after two or three weeks. |
| Ferric chloride | Unchanged cold. Traces of reduction to ferrous chloride after heating for several hours at 100°. |
| Potassium ferricyanide | Unchanged. |
| Ruthenium chloride | Unchanged. |
| Nitric acid, fuming* | Unchanged. |

*Comments.*—Russel (*J. Chem. Soc.*, 2, Vol. XII, p. 3) states that hydrogen reduces silver nitrate solution, nitric acid being at the same time reduced to nitrous acid. Pellet (*Compt. Rend.*, LXXVIII, p. 1132) finds that this reduction is due to the silver salt containing $Ag_2O$ in excess, but that perfectly neutral silver nitrate is not altered. In a series of experiments I have obtained results corroborating those of Pellet. Silver nitrate containing a minute trace of free nitric acid is not altered by hydrogen. If some freshly precipitated and washed silver oxide is digested with solution of silver nitrate, and the liquid then filtered, it will have an alkaline reaction towards litmus and is slowly reduced by hydrogen. Boiling the solution with silver oxide increases its alkalinity and also its sensitiveness towards hydrogen. As a reagent for the recognition of hydrogen, it is better that the solution of silver nitrate should be slightly basic (alkaline).

As regards the action of hydrogen upon ferric chloride, it should be said that mere traces of ferrous chloride are produced, as indicated by a faint change of color upon addition of potassium ferricyanide.

Free hydrogen has, therefore, a considerable reducing power for some of the more easily reducing metallic salts, which is intensified in some cases by heating to 100°.

It is convenient to distinguish between three classes of gas reactions as regards intensity.

Reactions of the first class, in which a change is prompt and quantitative in its results, *e. g.*, when carbon dioxide is brought into contact with soda solution.

Reactions of the second class, in which a change is slow but no less complete in a somewhat longer interval of time; *e. g.*, the reduction of platinum chloride solution by hydrogen.

Reactions of the third class, in which a change is not recognizable until after a considerable interval of time, and the products appearing then are only found in traces, such as the reduction of ferric chloride by hydrogen.

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* Winkler, *Zeit. Anal. Chem.*, 1889, p. 269.

None of the preceding reactions of hydrogen appear to fall under the first class. Nearly all are of the second class. That reactions such as I have called the third class should occur is difficult of explanation, and it is questionable whether a parallel is to be found in the case of ordinary reactions of metallic salts, *e. g.*, precipitation of traces of ferrous sulphide in ferrous chloride solution by hydrogen sulphide, or calcium oxalate by ammonium oxalate in dilute acid solution, where a change in the proportion of free acid or alkali may cause the precipitation to become complete. The reduction of ammoniacal silver solution by hydrogen cannot be materially accelerated by increase of ammonia or other change in the conditions, and thus remains a typical reaction of the third class, no matter how it is carried out.

### 2. *Reactions at High Temperatures.*

The heat of formation of hydrogen chloride being high (22 calories), it seemed probable that hydrogen should reduce the chlorides of many of the metals at moderate temperatures. Small quantities of metallic chlorides were heated in a slow current of hydrogen in a glass tube in the iron oven. The following reactions were observed:

| | TEMPERATURES OF REDUCTION. |
|---|---|
| Ruthenium chloride, anhydrous | 190°. |
| Gold chloride (obtained by evaporation of a solution of gold in aquaregia to dryness). | Not reduced at 300°. |
| Rhodium chloride, anhydrous | 200°. |
| Platinum chloride (obtained by evaporation of the solution of platinum in aquaregia to dryness). | Gave off hydrogen chloride and water at 150°. Not reduced at 300°. |
| Palladium chloride | Reduced cold. |
| Silver chloride | 270°–280°. |
| Silver bromide | 330°–360°. |
| Silver iodide | 350°–370°. |
| Mercuric iodide | Volatile without reduction. |

In the above experiments the hydrogen, after passing the heated metallic chloride, was conducted into dilute silver solution and the temperature observed at which a precipitation occurred. The reduction of palladium chloride occurs at the ordinary temperature. It is an exothermic change, as the following equation shows:

$$2\,PdCl_2 + 5\,H = Pd_2H\,^* + 4\,HCl$$
$$-\,(2 \times 40\ \text{Cal.}) + 9.4\ \text{Cal.} + (4 \times 22\ \text{Cal.}).$$

Hence the heat of the completed reaction will be 17.4 calories.

If hydrogen be passed over palladium chloride contained in a glass tube, an immediate reduction to metallic palladium occurs, attended by evolution of hydro-

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[*] The composition of palladium hydride is probably $Pd_2H$, according to Mendeleef, *Principles of Chemistry.* Vol. II, p. 355.

chloric acid. The reaction begins and is completed without application of external heat, the temperature of the mass becoming very high, as the above equation would indicate. The production of hydrogen chloride in this reaction renders palladium chloride a reagent of great sensitiveness for the recognition of free hydrogen in gas mixtures. In order to study the reaction more fully it was necessary to prepare pure, dry palladium chloride. When a solution of palladium in aquaregia is evaporated to dryness, brown amorphous crusts are formed which are very imperfectly soluble in water or hydrochloric acid. Analyses were made of the compound so obtained, but the results showed varying amounts of chlorine and it was evident that the salt had been partially decomposed during the evaporation. In order to obtain pure palladium chloride the following method of preparation was adopted.

Palladium dissolved in aquaregia was heated for several days in a covered beaker over the water bath. Hydrochloric acid was added from time to time to insure the destruction of any lower oxides of nitrogen. The solution was then evaporated to dryness and the residue heated to 180° in a glass tube through which a current of dry hydrogen chloride was passed. The excess of hydrogen chloride was then expelled by a stream of carbon dioxide, and after the escaping carbon dioxide was found to carry with it no more hydrogen chloride the compound was considered pure. Hydrogen was now passed through the tube and into standard soda solution. The palladium chloride was then reduced and the resulting hydrogen chloride absorbed by the soda. The chlorine was determined volumetrically. Two analyses were made. The results showed the salt to consist of palladium dichloride.

Experiments undertaken for the purpose of comparison of the properties of the two preparations demonstrated that palladium chloride prepared by the method above detailed is a much more sensitive reagent towards free hydrogen than the compound obtained on merely evaporating to dryness a solution of palladium chloride on the water bath. So delicate is the reaction that a neutral gas, such as nitrogen, containing 1-20 of 1 per cent. of free hydrogen, will rapidly give an indication when passed over the palladium chloride and into a solution of silver nitrate. It is absolutely necessary, especially where traces of hydrogen are suspected, that the gas should be dry, as moisture is liable to condense with the hydrogen chloride in drops, and thus the hydrogen chloride may be prevented from reaching the silver nitrate solution.

Ethylene reduces palladium chloride at temperatures above 100°.

The double chloride of palladium and potassium, $PdCl_2$ 2 KCl, is reduced at about 300° by ethylene.

The hydrocarbons of crude gasolene do not reduce palladium chloride at 190°.

Coal gas which had been stored under pressure in an iron cylinder, and which had lost all its original free hydrogen, did not reduce palladium chloride at 100°.

Pure methane (prepared by Gladstone and Tribe's method) exerted no action until heated nearly to 250°.

Palladium chloride heated in an inert gas, such as carbon dioxide, was found to yield chlorine at about 250°. In presence of oxygen the case is very different. Palladium chloride heated in dry air loses chlorine readily at 160°, being apparently converted into an oxychloride. After long-continued heating to 100° in air, chlorine in minute traces is set free and recognizable by silver nitrate containing some ferrous sulphate.

If air containing any hydrocarbon (paraffin, olefene or acetylene) be led over gently heated palladium chloride a decomposition occurs at once. The palladium salt is reduced and hydrogen chloride is promptly set free. Alcohol, ether and benzol vapor cause similar results. Repeated trials have shown that less than 0.1 per cent. of hydrogen in air may be recognized by the reaction above described if the temperature of the palladium chloride is not increased above 50° C. If the temperature rises to 100°, chlorine will be evolved from palladium chloride by the action of air alone, as may be easily shown by causing the air to bubble through silver nitrate solution containing a little ferrous sulphate (free chlorine is not easily detected by silver nitrate alone, and may bubble through it unabsorbed and unrecognized).

The reduction of anhydrous ruthenium chloride by hydrogen is curiously influenced by the presence of oxygen. Ruthenium chloride was reduced by pure hydrogen at 190°. In another experiment, using a mixture of hydrogen 4 volumes and air 6 volumes, no hydrochloric acid was produced, even on heating to 320°. The following is the most convenient method of applying the test:

The gas, previously dried (1) by calcium chloride and (2) by phosphoric anhydride, is conducted through a narrow tube to the bottom of a dry test-tube containing about 0.2 gm. of palladium chloride. The test-tube has a rubber cork with two holes. Through a second tube the gas escapes and passes into a solution of nitrate of silver. The test-tube may remain cold, but, in the absence of oxygen or air, it is better to immerse in water at 40° or 50°, provided no hydrocarbons likely to reduce palladium chloride are suspected. The palladium chloride may be placed in a glass tube of one-eighth-inch bore, with asbestos plugs to prevent its becoming displaced by the gas stream, and then the tube connected with the vessel containing silver nitrate solution. If traces only of hydrogen are to be tested for, oxygen must be completely removed by prolonged contact with pyrogallol and soda, or better with green vitriol solution and milk of lime. The latter method for the removal of oxygen is to be preferred, although the action is much slower.

Palladium oxidized by heating in air is quickly reduced by free hydrogen.

If a gas containing hydrogen is conducted over palladium oxide and then through a narrow tube containing a very small quantity of a mixture of potassium ferricyanide and green vitriol in fine powder, the moisture, formed in the reaction between the hydrogen and the palladium oxide, will change the color of the powder to blue.

Silver oxide is reduced by hydrogen at 100° (Darvidowa, *Ber.*, 1888, p. 442, R).

Iodic acid is not reduced by hydrogen at 250°, *i. e.*, at a temperature approaching the point at which iodic acid dissociates (distinction between hydrogen and carbon monoxide).

Iridium dioxide undergoes a reduction to metal in contact with free hydrogen. The reduction occurs in the cold and is attended with brilliant scintillations.

By employing a moisture indicator it is possible, by the help of this reagent, to recognize minute quantities of hydrogen.

In point of delicacy the palladium chloride reaction is superior to all others. Experiments are in hand with a view to the utilization of this reaction for the quantitative determination of hydrogen.

The occlusion of hydrogen by the reduced palladium and consequent loss have, so far, prevented the use of this reaction for quantitative work.

## METHANE.

*Preparation.*—From methyl iodide by the method of Gladstone and Tribe (see p. 157).

Methane, the typical member of the paraffin group, is (with the possible exception of ethane) the most stable towards reagents of all hydrocarbons.

### 1. *Reactions in Solution.*

| REAGENT. | REACTIONS. |
|---|---|
| Palladium chloride | The solutions of these salts are unaltered by prolonged contact with methane, cold or at 100°. |
| Platinum chloride | |
| Gold chloride | |
| Silver nitrate | |
| Ammoniacal silver nitrate | |
| Iridium chloride | |
| Rhodium chloride | |
| Cerium dioxide dissolved in sulphuric acid | |
| Potassium bichromate acidulated with sulphuric acid | |
| Mercuric chloride | |
| Ferric chloride | |
| Ruthenium chloride | |

Potassium permanganate (2 per cent. solution) is unchanged whether neutral or acidulated by sulphuric acid.

Osmic acid is not reduced by methane in the cold.

Potassium ferricyanide is unchanged.

Peroxide of hydrogen mixed with lime water remains clear, proving that no oxidation to carbon dioxide occurs.

Calcium hypobromite solution remains free from any deposit of calcium carbonate.

Bromine water is not discolored after prolonged contact.

Chlorine attacks methane only at a temperature considerably above 100°. A mixture of methane and chlorine was exposed over water to bright sunlight on a July day without undergoing any noticeable contraction in volume or change of color (see experiments in "Chlorination of Methane").

Potassium rutheniate is slowly reduced with separation of metallic ruthenium.

If methane is conducted into strong sulphuric acid to which crystals of permanganate have been added, immediate oxidation to carbon dioxide occurs, as proved by the action upon lime water (in this experiment stoppers made of plaster of Paris were used). This reaction towards permanganic anhydride is a very delicate one. All hydrocarbon gases yield a similar result.

### 2. *Reactions at High Temperatures.*

Ferric oxide (prepared by ignition of ferric nitrate) heated in a glass tube over a strong Bunsen burner flame underwent very slow and incomplete reduction, some carbon monoxide being formed in addition to carbon dioxide. Iodic acid (crystals) is not reduced by methane on heating nearly to its temperature of dissociation (250°). No iodine vapors and no carbon dioxide is formed. The action of methane upon the chloride, bromide and iodide of silver was tried by the same method followed in the case of hydrogen—these substances contained in a glass tube being heated in methane and the gas then conducted into silver nitrate solution. The temperatures of decomposition were as follows:

| | TEMPERATURE OF DECOMPOSITION. |
|---|---|
| Silver chloride | At melting point of Ba $(ClO_3)_2$ (414°). |
| Silver bromide | Above melting point of TlI (439°). |
| Silver iodide | Slightly volatile without reduction. |

The order of reducibility by hydrogen and by methane is the same, therefore, as in the case of the action of light, the chloride being the most easily reduced, the iodide the most stable.

Nickel chloride heated in natural gas (from Murrysville) underwent conversion into its nearly colorless beautifully crystalline modification.

An analysis made in the laboratory by Mr. H. T. Weed showed the composition of the salt to have been unchanged. At a dull red heat reduction occurred, with liberation of carbon.

## ETHANE.

This hydrocarbon was prepared from ethyl iodide by the process of Gladstone and Tribe, as described on p. 159.

### 1. *Reactions in Solution.*

All the reagents used in the case of methane were tried. The reactions were so closely similar that a detailed statement is omitted as unnecessary.

Ethane exhibits the same stability as the other paraffins towards reagents in solution. Oil of vitriol containing crystals of potassium permanganate causes prompt oxidation to carbon dioxide.

Potassium rutheniate is quickly reduced with separation of metallic ruthenium.

### 2. *Reactions at High Temperatures.*

Towards iodic acid, silver bichromate and the various metallic oxides, ethane closely resembles methane in its reactions.

## PROPANE.

### *Reactions.*

Experiments with propane, made by the method of Gladstone and Tribe from propyl iodide, led to results closely similar to those obtained with ethane and methane.

As already stated, propane is somewhat more easily oxidized than the paraffins lower in carbon. In a series of trials, using the same reagents in solution as mentioned in the preceding experiments, no reactions were obtained which would serve to distinguish between propane and methane or ethane. The results are therefore omitted.

## ISOBUTANE.

### *Reactions.*

This hydrocarbon, prepared by the method of Gladstone and Tribe from isobutyl iodide, was found to closely resemble the paraffins already described in its reactions. It is characterized, however, by a lower oxidation temperature, as already stated, in regard to the experiments with palladium asbestos.

### HEPTANE.

Heptane obtained from theoline (see p. 161) was found to have the same general chemical properties as methane. Even cerium dioxide, osmic acid, gold chloride and potassium permanganate are unaltered by prolonged contact with the liquid hydrocarbon. Heptane seems in fact to be almost, if not quite, as stable as methane towards reagents in solution.

The paraffins as a group are, in the main, so proof against reactions that we can do little more than remove all other hydrocarbons by suitable reagents and then test for paraffins by combustion over oxide of copper to carbon dioxide and water. This, of course, leaves the nature of the individual paraffins undetermined.

Spongy palladium, heated in air so as to become partially converted to palladium oxide and transferred to an atmosphere of methane or other paraffin, undergoes a reduction. The reduced metal then combines with the carbon of the hydrocarbon (Graham and Otto, Vol. III, p. 995; Wilm, *Ber.*, 1892, p. 220). This carbide heated in air or oxygen yields carbon dioxide. The production of carbon dioxide in this case may be utilized as a test for hydrocarbons in a gas mixture, provided no free oxygen is present. The carbide of palladium, formed by the above method, dissolves in aquaregia (containing but little nitric acid) with a camphor-like odor.

### OLEFINES: ETHYLENE.

For preparation, see p. 161. The method of Erlenmeyer and Bunte was used. It is necessary for the purpose of studying its reactions to purify the gas from traces of alcohol and ether vapor by prolonged digestion with sulphuric acid.

#### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Quickly reduced, the metal appearing as a black powder. No carbon dioxide is formed. |
| Platinum chloride | Unchanged. |
| Gold chloride | Extremely slow reduction, the gold appearing as a brown powder. No carbon dioxide. |
| Gold chloride in excess of potassium hydroxide | Extremely slow reduction. |
| Iridium chloride | Unchanged. |
| Ruthenium chloride | After prolonged contact (several days) the solution is bleached. No deposition of metal occurs. |
| Rhodium chloride | Unchanged. |
| Silver nitrate | Unchanged. |
| Silver nitrate in ammoniacal solution | Unchanged. |
| Potassium permanganate, neutral solution | Quickly turns brown. |

| | |
|---|---|
| Potassium permanganate acidulated with sulphuric acid. | Quickly bleached. |
| Potassium permanganate crystals in concentrated sulphuric acid. | Prompt oxidation to carbon dioxide. |
| Potassium bichromate acidulated with sulphuric acid .. | No change of color, cold or at 100°. |
| Osmic acid........................................ | Quickly reduced, with separation of metal as a black powder. |
| Potassium rutheniate.............................. | Quickly reduced, with separation of metal. |
| Ferric chloride.................................... | No change, cold or at 100°. |
| Calcium hypobromite containing excess of lime water.. | No precipitation of calcium carbonate, and hence no oxidation to carbon dioxide. |
| Potassium ferricyanide............................ | Unchanged. |
| Bromine water..................................... | Rapid but incomplete absorption. |
| Peroxide of hydrogen.............................. | No oxidation to carbon dioxide. |

### 2. *Reactions at High Temperatures.*

Silver oxide is reduced by ethylene with simultaneous formation of silver carbonate at 140° (Darvidowa, *Ber.*, 1888, p. 442, R). Palladium chloride (dry) is reduced at about 140°. Iodic acid is reduced with liberation of iodine at about 270°.

*Comments.*—As is well known, bromine vapor and ethylene combine to form an oily liquid by the reaction so characteristic of the olefine group. Winkler (*Fres. Zeitschr.*, 1889, p. 269) has shown that the absorption of ethylene by bromine is incomplete, and that the contraction in volume is by no means proportional to the volume of the ethylene present.

I have tried experiments upon $C_2H_4$ from alcohol and from ethylene dibromide (by the action of zinc powder) and the results show that a considerable residue of hydrocarbon remains unabsorbed after prolonged contact with bromine water in sunlight. The residual gas, on being mixed with air and passed over ignited oxide of copper, gave carbon dioxide and water at the outset.

The reaction between ethylene and palladium chloride in solution is of the second class and complete, the gas being rapidly absorbed. Palladium is deposited as a black powder, but no trace of oxidation to carbon dioxide occurs. The reaction is almost the same in the cold and at 100°. The gas escaping from the palladium chloride solution (after complete reduction to metallic palladium) produces no precipitate in lime water. The reaction between palladium chloride and ethylene leads to the production of aldehyde (a study of the changes here involved is yet in hand). Of especial interest in this connection is a statement by Berthelot, that ethylene is oxidized to aldehyde by the action of chromic acid solution at 120° (*Compt. Rend.*, Vol. CXVIII, p. 334).

Gold chloride produces a similar result, the metal being slowly reduced. As in the case of palladium chloride, no carbon dioxide is formed.

Rhodium chloride is remarkably stable towards ethylene (and other olefines); after three months' contact with the gas, no trace of reduction was observed.

Potassium permanganate (in weak solution) has been shown by Wagner (*Ber.*, Vol. XXI, p. 1230) to convert olefines on digestion (cold) into glycols. The reaction may serve as a mode of preparing glycols, but could only in exceptional cases be utilized as a gas reaction.

Chromic acid mixture is said to be reduced by ethylene (Chapman and Thorp, *Watt's Dic.*, 1st Supp., p. 602). In repeated experiments I have failed to show that chromic acid undergoes reduction by ethylene. No carbon dioxide is formed, the color of the solution remains unchanged, and no absorption occurs on prolonged contact of ethylene with a 10 per cent. solution of chromic acid in a eudiometer. Similar results were obtained in using potassium bichromate acidulated by sulphuric acid. Carbon dioxide could not be detected on passing ethylene through a solution of chromic acid at 100°.

Potassium rutheniate, an extremely sensitive reagent, loses its orange color rapidly and deposits metallic ruthenium.

Peroxide of hydrogen is said by Berthelot to convert ethylene into glycol. This has apparently no significance as a gas reaction.

The reduction of palladium chloride solution, if *not* attended by evolution of carbon dioxide, is an evidence of the presence of an olefine (and probably ethylene as the commonest of the olefines) in a gas mixture.

Sulphuric acid does not absorb ethylene in the cold, but the absorption is rapid at a temperature of 160°.

## PROPYLENE.

*Preparation.*—From allyl iodide by the action of zinc (see p. 165).

### 1. *Reactions in Solution.*

Propylene, in its reactions towards the various reagents, resembles ethylene so closely that no important differences can be mentioned.

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Reduction is prompt and complete, the gas undergoing rapid absorption. If mixed with nitrogen (as an inert diluent) and conducted into lime water, after passing through the palladium chloride solution, it is easily shown that no oxidation to carbon dioxide is produced by the palladium chloride. The same is true if air is used instead of nitrogen. |
| Platinum chloride solution | Unchanged, cold or at 100°. |

| | |
|---|---|
| Gold chloride | No change cold; until after prolonged contact or on heating to 100°. |
| Silver nitrate | Unchanged. |
| Silver nitrate in ammoniacal solution | Unchanged. |
| Iridium chloride | Unchanged, cold or at 100°. |
| Ruthenium chloride | Unchanged. |
| Rhodium chloride | Unchanged. |
| Potassium rutheniate | Traces of reduction after twenty-four hours. |
| Cerium dioxide in dilute sulphuric acid | No change, cold or at 100°. |
| Potassium permanganate | Slowly turns brown. |
| Potassium permanganate acidulated with dilute sulphuric acid. | Quickly bleached. |
| Potassium permanganate crystals in concentrated sulphuric acid. | Prompt oxidation to carbon dioxide. |
| Chromic acid | Unchanged. |
| Osmic acid | Quickly reduced, with precipitation of metal as a black powder. |
| Ferric chloride | Unchanged, cold or at 100°. |
| Bromine water | Incomplete absorption, even after prolonged contact. |
| Peroxide of hydrogen | No carbon dioxide formed. |
| Ferricyanide of potassium | Unchanged. Not reduced to ferrocyanide. |
| Calcium hypobromite containing excess of lime water | Unchanged. |
| | Propylene is not absorbed by sulphuric acid in the cold. |

## 2. *Reactions at High Temperatures.*

As regards reducing action upon metallic oxides, no important properties distinguishing propylene from ethylene can be named.

Propylene conducted over crystals of iodic acid contained in a glass tube heated in the oven undergoes oxidation, yielding iodine vapors and carbon dioxide at a temperature approximating that of dissociation of the iodic acid.

*Comments.*—Towards reagents in solution, propylene appears in some cases to possess slightly greater stability than ethylene. This is especially the case with gold chloride and potassium rutheniate. Like ethylene, it is not oxidized to carbon dioxide by any of the reagents used in solution, with the exception of potassium permanganate in concentrated sulphuric acid. Experiments with bromine water have led to the same results as in the case of ethylene. The absorption is decidedly incomplete.

### ISOBUTYLENE.

This gas was prepared from isobutyl iodide by the method described on p. 167. The reactions were in the majority of cases perfectly similar to those of ethylene and propylene.

### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Quickly reduced. No carbon dioxide is formed. |
| Platinum chloride | Unchanged. |
| Gold chloride | Quickly reduced. No carbon dioxide is evolved in the cold or at 100°. |
| Silver nitrate | Unchanged. |
| Ammoniacal silver nitrate | Unchanged. |
| Rhodium chloride | Unchanged. |
| Potassium rutheniate | Quickly reduced. |
| Cerium dioxide in dilute sulphuric acid | Rapidly bleached. |
| Potassium permanganate, neutral | Turns brown. |
| Potassium permanganate acidulated with dilute sulphuric acid. | Quickly bleached. |
| Potassium permanganate crystals in concentrated sulphuric acid. | Prompt oxidation of the gas to carbon dioxide. |
| Chromic acid solution | Unchanged. |
| Osmic acid | Quickly reduced, metallic osmium being precipitated. |
| Ferric chloride | Unchanged. |
| Bromine water | Promptly but incompletely absorbed. |
| Peroxide of hydrogen | No formation of carbon dioxide. |
| Potassium ferricyanide | Unchanged. |
| Calcium hypobromite containing excess of lime water | Unchanged. |
| Iodine dissolved in iodide of potassium solution | Quickly bleached. |
| Mercurous nitrate | Precipitation of a gray powder which consists of (or changes into) metallic mercury. |
| Sulphuric acid of 1.8 specific gravity | Does not absorb isobutylene in the cold. |

### 2. *Reactions at High Temperatures.*

Experiments upon the reducing action of isobutylene upon metallic oxides at high temperatures did not develop any characteristic differences.

Iodic acid was reduced by isobutylene at 89°, with formation of carbon dioxide and free iodine.

*Comments.*—Isobutylene prepared by Puchot's method from isobutyl alcohol causes a white precipitate in ammoniacal silver nitrate solution, while that prepared from isobutyl iodide and potash exerts no such action.

The reaction towards mercurous nitrate (of the second class) distinguishes between isobutylene and the olefines lower in carbon. In its bleaching action upon iodine dissolved in iodide of potassium solution, isobutylene differs from both ethylene and propylene and also in the fact that it bleaches cerium dioxide in sulphuric acid solution. It is not oxidized to carbon dioxide by any of the reagents in solution, with the exception of permanganate of potash in strong sulphuric acid.

### TRIMETHYLENE.

This hydrocarbon was prepared from trimethylene bromide by the action of zinc (see p. 166). The gas was purified by sulphuric acid and by digestion with dilute potassium permanganate solution.

### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Reduced with extreme slowness. No carbon dioxide is formed. The reaction requires a much longer time than in the case of the olefines proper. |
| Platinum chloride | Unchanged, cold or at 100°. |
| Gold chloride | Unchanged, cold or at 100°. |
| Silver nitrate | Unchanged. |
| Ammoniacal silver nitrate | Unchanged. |
| Iridium chloride | Unchanged, cold or at 100°. |
| Rhodium chloride | Unchanged, cold or at 100°. |
| Potassium rutheniate | Traces of reduction after prolonged contact (reaction of the third class). |
| Cerium dioxide dissolved in dilute sulphuric acid | Unchanged. |
| Potassium permanganate, neutral | Unchanged. |
| Potassium permanganate acidulated with dilute sulphuric acid. | Unchanged. |
| Potassium permanganate crystals in sulphuric acid | Immediate oxidation to carbon dioxide. |
| Chromic acid | Unchanged. |
| Ferric chloride | Traces of reduction to ferrous chloride after twenty-four hours (reaction of the third class). |
| Bromine water | Extremely slow absorption. |
| Peroxide of hydrogen | Unchanged. |
| Potassium ferricyanide | Unchanged. |
| Calcium hypobromite in excess of lime water | Unchanged. |
| Iodine dissolved in potassium iodide solution. | Unchanged. |
| Sulphuric acid, 1.8 specific gravity | The gas is not absorbed in the cold. |

### 2. *Reactions at High Temperatures.*

Iodic acid in crystals was reduced with formation of carbon dioxide at a temperature closely approximating the temperature of dissociation of the acid.

*Comments.*—The olefines are characterized by great stability towards oxidizing influences at temperatures below 100°, so that carbon dioxide is not evolved except in the case of the action of potassium permanganate in concentrated sulphuric acid. In several cases where destructive oxidation might be expected to occur, the olefines are converted into glycols (*e. g.*, in the case of dilute potassium permanganate).

Trimethylene yields reactions similar to those of the true olefines but is decidedly more stable towards many reagents. It does not reduce osmic acid, potassium permanganate or gold chloride. By these three reagents it is best distinguished from the true olefines.

It may be mentioned that ether vapor, which so frequently contaminates the olefines, does not reduce palladium chloride solution.

## CARBONIC OXIDE.

This gas was prepared by heating a mixture of pure oxalic acid and sulphuric acid and purified by caustic soda solution.

### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Quickly reduced, with oxidation of carbon monoxide to carbon dioxide. The reaction is very delicate in strongly acid solutions or in solutions of the pure, dry chloride in water. |
| Platinum chloride | Carbon monoxide is oxidized to carbon dioxide, cold or at 100°. A reduction of the platinum salt to a lower chloride occurs, the solution assuming a darker color. After prolonged contact (several days or even weeks) an incomplete precipitation sometimes, but not always, occurs. |
| Gold chloride | Quickly reduced to metallic gold in form of a brown powder, the carbon monoxide being rapidly oxidized to carbon dioxide, cold or at 100°. |
| Gold chloride in excess of potassium hydroxide | Immediately reduced. Very delicate reaction (of the first class). |
| Silver nitrate | Unchanged. |
| Ammoniacal silver nitrate | Slow reduction to metallic silver, which separates as a black powder. The filtrate from the precipitated silver was found to contain nitrous acid (as a result of the action of the carbon monoxide on silver nitrate in ammonia) when tested by Griess' reaction. |
| Iridium chloride | Slowly reduced to metal. |
| Rhodium chloride | Unchanged cold; slowly reduced at 100° (reaction of the third class). |
| Potassium rutheniate | Rapidly reduced. Metallic ruthenium separates as a black powder. |
| Cerium dioxide in dilute sulphuric acid | Unchanged, cold or at 100°. |
| Potassium permanganate | Quickly reduced, whether in neutral, alkaline or acid solution. |
| Chromic acid | No change of color occurs, but a trace of carbon dioxide is formed (reaction of the third class). |
| Osmic acid | Quickly reduced. |
| Ferric chloride | Ferrous chloride is produced in traces after prolonged contact. |
| Hydrogen peroxide | No oxidation to carbon dioxide. |

| | |
|---|---|
| Ferricyanide of potassium | Unchanged. |
| Calcium hypobromite containing excess of lime water | Unchanged. |
| Fuming nitric acid | Oxidation to carbon dioxide. |

## 2. *Reactions at High Temperatures.*

Iodic acid in crystals is reduced by carbon monoxide, yielding carbon dioxide and iodine vapors at 90° (De La Harpe, *Fres. Zeitschr.*, 1889, p. 391). De La Harpe recommends this method for the recognition of carbon monoxide in air. As higher olefines reduce iodic acid at about the same temperature as carbon monoxide, it would be necessary to remove them. According to my experiments, it would be necessary also to remove acetylenes, benzol and alcohol vapors, inasmuch as these substances exert an action similar to that of olefines. The lower paraffins are without action up to temperatures at which iodic acid dissociates.

Potassium iodate in crystals is not reduced by carbon monoxide at the melting point of barium nitrate (593°). Carbon monoxide undergoes a decomposition in presence of certain metals at high temperatures, according to the reaction:

$$2\,CO = CO_2 + C.$$

Nickel causes such a change to occur at 350°, a very small quantity of the metal serving to decompose a large volume of the gas (Mond. and Quincke, *Chem. News*, 1891, p. 108). Iron is said to cause a similar decomposition at 227° (Bell, *Chemical Phenomena of Iron Smelting*, pp. 80, 81). I have made the following experiment with palladium:

Palladium asbestos was heated in a porcelain tube in a slow stream of pure carbon monoxide, air having been expelled from the apparatus previous to the heating by means of the carbon monoxide stream. At a moderately high temperature (it was below redness) carbon dioxide was produced in such quantity as to cause a strong reaction in lime water.

Carbon monoxide reduces oxide of iron at 240°, according to Bell.

Howe (*Eng. and Min. J.*, L, p. 426) states that incipient reduction of iron oxide by carbon monoxide occurs at 141°.

The temperature of reduction of oxide of iron by carbon monoxide is unquestionably much lower than in the case of methane and ethane.

Carbonic oxide is absorbed by soda lime at a temperature of 200°–220°, yielding sodium formate. Moisture promotes the reaction (Merz and Weith, *Ber.*, 1880, p. 718). The reaction is as follows:

$$NaOH + CO = HCOONa.$$

The change is checked at higher temperatures, hydrogen being liberated at 300°. The volatile formic acid easily liberated from the sodium formate (by decomposition and distillation with tartaric acid) may be recognized by its reducing action upon ammoniacal silver nitrate solution. The purest caustic soda obtainable often contains substances of a reducing nature, and it is necessary to use soda free from such impurities. If the formate of soda extracted by water from the soda lime be acidulated and distilled, the formic acid obtained in the distillate may be tested for by silver solution.

Carbon monoxide is oxidized to carbon dioxide by steam alone, at 900° (Naumann and Pistor, *Ber.*, 1885, p. 2724).

### *Action of Carbon Monoxide upon Methane (Natural Gas) at High Temperatures.*

According to Odling (*Watt's Dic.*, Vol. I, p. 1111), the following reaction occurs when methane and carbon monoxide are passed through a heated tube:

$$CH_4 + CO = H_2O + C_2H_2.$$

Natural gas from Murrysville, Pa., having the following composition, was used in the experiment detailed below:

| | |
|---|---|
| Methane | 95.40 |
| Carbon dioxide | 0.20 |
| Nitrogen | 4.40 |
| | 100.00 |

Natural gas mixed with carbon monoxide in the proper proportion (both being carefully freed from $CO_2$) was passed through a porcelain tube filled with bone-black (previously purified from lime salts by muriatic acid).

The tube was heated by a coke fire with a strong draft to a temperature which finally caused softening of the porcelain tube. The escaping gases were passed (1) into lime water, (2) into ammoniacal cuprous chloride. No trace of a red precipitate appeared in the cuprous chloride solution such as would have formed if acetylene had been produced. On replacing the cuprous chloride solution by bromine water, no oily drops collected in the fluid such as would have formed if an olefine had been produced. I have failed, therefore, to show that methane in contact with carbon monoxide at a high temperature gives rise to the formation of an unsaturated hydrocarbon.

*Comments.*—The best reagent for the recognition of carbon monoxide is palladium chloride. The reaction towards this salt in solution forms the basis of the well-known method for the quantitative determination of carbon monoxide. Although slow, the reaction is extremely delicate. It is accelerated by warming to 100°. Minute quantities of carbon monoxide in air may be recognized by the precipitation of metallic palladium from palladium chloride solution. The precipitation often appears in the form of a lustrous metallic film of dark brown color coating the glass. My experiments upon the action of olefines show, however, that it is essential to the identification of carbon monoxide that the formation of carbon dioxide by the action of the palladium chloride be proved by means of lime water or other indicator, as otherwise the reduction of the palladium salt may be due to a member of the olefine group. The air may be caused to flow slowly through palladium chloride solution and then into lime water. The tendency to undergo oxidation to carbon dioxide on the part of carbon monoxide, and the absence of such tendency on the part of the olefines when exposed to oxidizing influences at a temperature of 100° or below, serves as a most important criterion for the purpose of distinguishing between CO and the olefine group. Winkler (*Fres. Zeit.*, 1889, p. 269) has called attention to the value of palladium chloride as a reagent for the detection of carbon monoxide and has made many valuable suggestions. (For a very convenient form of apparatus for the quantitative determination of carbon monoxide by palladium chloride, see Ellen Richards, *Am. Chem. Jour.*, Vol. VII.)

Platinum chloride is also a valuable reagent for the detection of carbon monoxide. Although oxidation to carbon dioxide occurs, no metal is precipitated unless the exposure to the gas be continued for several days, when traces of platinum appear. The solution assumes a darker color and a partial reduction results.

Gold chloride solution is as energetic as palladium chloride in causing oxidation of carbon monoxide.

The reduction of ammoniacal nitrate of silver solution by carbon monoxide has been described by Berthelot (*Compt. Rend.*, CXII, p. 597). Although chromic acid produces minute traces of carbon dioxide at 100° when carbon monoxide is conducted through its solution, my results do not confirm the statements of Ludwig (*Ann. Ch. Pharm.*, CLXII, p. 47), according to whom carbon monoxide may be determined by oxidation to carbon dioxide caused by chromic acid solution.

The interesting compound formed by the direct union of carbon monoxide and platinum chloride (Pullinger, *J. Ch. Soc.*, 1891, p. 598) is not likely to prove of importance in connection with the study of gas reactions.

Among the reactions I have studied, the most important for distinguishing between olefines and carbon monoxide are the following:

(1) The action of palladium chloride, which in the case of carbon monoxide

yields carbon dioxide and in the case of ethylene yields no carbon dioxide. In both cases reduction of the palladium salt occurs.

(2) Ammoniacal silver nitrate is unaltered by olefines up to and including $C_4$, but is reduced to metallic silver and ammonium nitrite by CO.

(3) Platinum chloride yields carbon dioxide, but is not immediately reduced to metal by CO. With $C_2H_4$ no change occurs.

(4) Rhodium chloride is slowly reduced by CO, but is unaltered by $C_2H_4$.

(5) Ruthenium chloride is bleached by carbon monoxide without reduction to metal. Upon ethylene it exerts no action in the cold, but at 100° is slowly bleached. No precipitation occurs in either case. Like palladium chloride, it converts ethylene into aldehyde, especially on warming to 100°.

Among olefines, isobutylene is distinguished by its reducing action upon cerium dioxide and by its absorption of iodine in solution, the color of the latter being bleached.

Trimethylene, which is a saturated hydrocarbon, cannot be properly included among olefines although isomeric with them. It is especially distinguished from the olefines proper by its stability towards neutral potassium permanganate and towards osmic acid. In almost all cases the reactions of trimethylene are much slower and less complete than those of the olefines.

## ACETYLENE.

This hydrocarbon was prepared by the action of alcoholic potash upon ethylene dibromide (see p. 167). The method of preparation proposed by Berthelot (*Ann. Ch. Phys.* (5) X, p. 365), by causing a Bunsen burner to "strike back," although applicable for coal gas, has not given satisfactory results when natural gas was used.

### 1. *Reactions in Solution.*

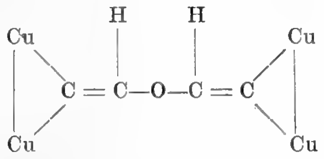
| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Reddish-brown precipitate. No reduction occurs. Very sensitive. |
| Platinum chloride | Unchanged, cold or at 100°. |
| Gold chloride | Immediate reduction. Intensely black precipitate of gold. No carbon dioxide formed. |
| Gold chloride in excess of potash | No change cold; trace of reduction at 100°. |
| Silver nitrate | White precipitate. Very delicate reaction. |
| Ammoniacal silver nitrate | White precipitate, which is so gelatinous that a 10 per cent. solution of silver nitrate becomes nearly solid, like boiled starch. |
| Iridium chloride | No change cold; reduction after one week, or on boiling. |
| Rhodium chloride | Unchanged. |
| Potassium rutheniate | Very slow reduction. |

| | |
|---|---|
| Cerium dioxide in dilute sulphuric acid | Slowly bleached. |
| Potassium permanganate | Turns brown at once. |
| Potassium permanganate in dilute sulphuric acid | Quickly bleached. |
| Potassium permanganate crystals in concentrated sulphuric acid. | The gas is immediately oxidized to carbon dioxide. |
| Potassium bichromate acidulated with sulphuric acid | The color is unchanged, cold or at 100°. |
| Osmic acid | Quickly reduced, turning black from precipitated metal. |
| Copper sulphate in neutral or ammoniacal solution | Unchanged. |
| Ferric chloride | Decided reduction to ferrous chloride, in twenty-four hours cold. |
| Calcium hypobromite containing excess of lime water. | Acetylene is slowly oxidized, yielding CO$_2$, the lime water becoming milky. |
| Hydrogen peroxide and lime water | The fluid remains clear. |
| Bismuth pentoxide in excess of caustic potash solution | Unchanged. |
| Potassium ferricyanide | Unchanged. |
| Iodine dissolved in potassium iodide solution | Unchanged. The color is not bleached. |
| Yellow oxide of mercury | Unchanged in color. |
| Mercurous nitrate | White precipitate. |
| Cuprous chloride in ammonia | Deep red precipitate, the well-known "copper acetylide." |
| Chromous chloride (CrCl$_2$) | Is said to absorb acetylene (Roscoe and Schorlemmer, Vol. II, Pt. II, p. 160). |
| Mercuric chloride | White precipitate. Very delicate reaction. This reagent converts acetylene into acetone (*Ber.*, XVII, p. 28, and XXI, p. 3344). |

### 2. *Reactions at High Temperatures.*

Iodic acid in crystals was found to be reduced by acetylene at about 90°. In this reaction iodine vapors and carbon dioxide appeared. Aside from the experiments on oxidation by finely divided metals already detailed, no other reactions at high temperatures were tried.

*Comments.*—Ammoniacal cuprous chloride, the absorbent commonly recommended for acetylene, although a very delicate reagent for the recognition of the gas, is at the same time slow and its action is liable to be incomplete. A single bubble of the gas will cause a decided red precipitate, but acetylene may be passed slowly through a series of Woulfe bottles containing the ammoniacal cuprous chloride solution and yet be very incompletely absorbed, so that it may still cause precipitation in the same reagent. The bright red precipitate dissolves easily in hydrochloric acid, with evolution of acetylene on boiling. This affords a convenient and well-known method for the purification of the gas. Exposed to the air, however, the red compound changes to a deep brownish black and becomes insoluble in acids. Consequently, in preparing and washing the red copper acetylide, with a view to its decomposition by hydrochloric acid which liberates the pure acetylene, great care is necessary to avoid exposure to the air (Keyser, *Am. Chem. Jr.*, 1892, p. 285). According to Berthelot, the copper compound is vinyl oxide in which copper has replaced hydrogen.



(*Bull Soc. Chim* (2), V, p. 191).

According to Keyser, the copper and silver compounds are $Cu_2C_2$ and $Ag_2C_2$.

Silver nitrate is probably the most sensitive reagent tried. Moreover, as the silver compound does not appear to be susceptible to oxidation, it may be used in testing for acetylene in the presence of air or oxygen, while the copper compound, on account of its strong tendency to undergo oxidation, is far less easily recognized in deeply colored copper solution. Potassium permanganate in concentrated sulphuric acid, calcium hypobromite and osmic acid are the only reagents which cause direct oxidation in the cold of acetylene to carbon dioxide. As an unsaturated hydrocarbon, its indifference towards iodine solution was somewhat unexpected in view of the avidity of isobutylene for iodine (see p. 193).

The prompt reduction of gold chloride forms a singular contrast to the indifference of platinum chloride towards acetylene. The color of the gold when precipitated by acetylene (usually blue or blue-black) is quite different from the brownish-yellow color so often observed when gold salts are reduced.

This difference in color of the precipitated gold is probably not due to rapidity of reduction.

### ALLYLENE.

This hydrocarbon was prepared from propylene bromide by the action of alcoholic potash. The gas resulting was washed by boiling alcoholic potash solution and absorbed by ammoniacal cuprous chloride. The yellow precipitate resulting was washed and afterwards decomposed by hydrochloric acid, allylene being then set free in a pure state.

### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Dark-brown precipitate, which may be preserved without decomposition. Closely resembles the precipitate produced by acetylene. |
| Platinum chloride | Unchanged. |
| Gold chloride | Slowly reduced. The color of the precipitated gold is very dark. |

| | |
|---|---|
| Silver nitrate | A 10 per cent. solution quickly coagulates to a white, curdy mass. The precipitate dissolves on boiling or on addition of ammonia. A very delicate reaction. |
| Ammoniacal silver nitrate | Unchanged. |
| Iridium chloride | Unchanged in the cold ; at 100° iridium is precipitated. |
| Rhodium chloride | Unchanged. |
| Potassium rutheniate | Slowly reduced. Black precipitation of metallic ruthenium. |
| Cerium dioxide dissolved in dilute sulphuric acid | Unchanged. |
| Potassium permanganate | Quickly turns brown. |
| Potassium permanganate in dilute sulphuric acid | Quickly bleached. |
| Potassium permanganate crystals in concentrated sulphuric acid. | Prompt oxidation to carbon dioxide. |
| Mercuric chloride | Dense white precipitate. Very delicate reaction. |
| Potassium bichromate acidulated with dilute sulphuric acid. | Unchanged in color. |
| Osmic acid | Reduced. Metallic osmium is deposited as a black powder. |
| Ferric chloride | Decided reduction to ferrous chloride. |
| Calcium hypobromite | Allylene is oxidized to carbon dioxide. The fluid grows milky. |
| Lime water and hydrogen peroxide | Unchanged. |
| Potassium ferricyanide | Unchanged. |
| Iodine dissolved in potassium iodide solution | Unchanged. |
| Cuprous chloride in excess of ammonia | Canary-yellow precipitate, changing slightly to greenish yellow on contact with air. Soluble in acids, with liberation of allylene. |
| Mercurous nitrate | White precipitate. |

### 2. *Reactions at High Temperatures.*

Experiments were tried in the reduction of certain metallic oxides, but the results are not of sufficient importance to be detailed here.

*Comments.*—The reactions of allylene closely resemble those of acetylene. As regards intensity, scarcely any difference can be found. The colors of the palladium compounds of acetylene and allylene do not differ materially. Towards ammoniacal cuprous chloride the two gases exhibit very characteristic differences as regards the color of the resulting compound. The copper allylide is easily soluble in dilute hydrochloric acid. Ammoniacal silver nitrate yields a gelatinous precipitate with acetylene but is not changed by allylene. Oxidation of allylene to carbon dioxide, as in the case of acetylene, is not easily effected except by the most powerful oxidizing agents, such as calcium hypobromite or potassium permanganate in concentrated sulphuric acid. Although the allylene copper compound is rapidly formed in an ammoniacal cuprous chloride solution, the absorption of the gas is singularly incomplete. Agitation with the solution is quite necessary in order to insure complete absorption. Wagner (*Ber.*, 1888, p. 3343) has shown that the higher acetylenes, like the olefines, are converted by neutral potassium permanganate solution into hydroxyl compounds.

The various classes of hydrocarbons of the fatty series possess in common a high resistance to destructive oxidation by oxidizing agents, yielding in some cases hydroxyl compounds but rarely $CO_2$. This is true also of benzene, which is changed by potassium permanganate into oxalic acid and formic acid (Bernthsen, p. 326).

## SULPHUR COMPOUNDS.

### CARBON OXYSULPHIDE.

This gas was prepared by the method of Klason (*Ber.*, 1887, p. 55 R, and *J. Pr. Ch.*, Vol. XXXVI, p. 64). To a cold mixture of 290 c.c. sulphuric acid and 400 c.c. of water, 50 c.c. of a saturated solution of sulphocyanide of potassium was gradually added, the mixture being warmed to 30°. The gas was evolved in a steady stream and was purified by passage (1) through 20 per cent. potash solution, (2) through 25 per cent. solution of aniline in alcohol, (3) through broken ice.

COS was also prepared by the action of carbon disulphide on alumina at a high temperature (Gautier, *Compt. Rend.*, CVII, p. 911). The gas, if dry, may be preserved over mercury. Contact with water causes a change into carbon dioxide and hydrogen sulphide. Caustic soda solution is changed into a mixture of sodium sulphide and carbonate. The constant tendency to decomposition renders it impossible to preserve the gas over water without loss. In trying its reactions, it was found necessary to conduct the gas immediately before use into some substance specially adapted to absorb hydrogen sulphide. For the absorption of $H_2S$, Fresenius recommends pumice saturated with copper sulphate solution and dried (Fresenius, *Quant. Analyse*, 6te Auflage). In a series of trials with this and other absorbents, precipitated oxide of mercury was found to answer best. Dampened absorbent cotton is coated with the yellow powder by rubbing with a large pestle. This preparation, used dry in a long glass tube, completely removes $H_2S$ but exerts no action upon COS.

### 1. *Reactions in Solution.*

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Prompt precipitation. Precipitate is brownish black and flocculent. |
| Platinum chloride | Black precipitate. |
| Gold chloride | Rapidly darkens. An olive-brown precipitate collects. |
| Copper sulphate | Black precipitate, which forms very slowly. |
| Ammoniacal copper sulphate | Black precipitate, forming promptly. |

| | |
|---|---|
| Silver nitrate | Voluminous, brownish black precipitate. |
| Ammoniacal silver nitrate | Prompt precipitation. |
| Cadmium chloride | Precipitation is slow and incomplete. |
| Cadmium chloride in excess of ammonia | Rapid and complete precipitation; bright yellow. |
| Arsenious chloride | Yellow precipitate, forming very slowly. |
| Potassium permanganate acidulated by hydrochloric acid. | Rapidly bleached. The solution then precipitates barium chloride, so that oxidation to sulphuric acid has occurred. No separation of sulphur is observed. |
| Lead acetate | Black precipitate. |
| Bromine water | Prompt oxidation to sulphuric acid. No sulphur is separated. |
| Mercuric nitrate | Turns milky white and darkens gradually to black. |
| Nickel hydrate in water | Darkens slowly to black. |
| Ferric chloride | Decided but incomplete reduction to ferrous chloride. |
| Potassium ferricyanide | Traces of reduction to ferrocyanide. |
| Osmic acid | Rapidly reduced. |
| Potassium rutheniate | Rapidly blackened. |
| Cerium dioxide in dilute sulphuric acid | Rapidly bleached. |
| Yellow oxide of mercury | These are all unchanged if dry. Sealed in a glass tube filled with the gas for two months, no change had occurred. If spread upon cotton, these substances may be used to remove sulphuretted hydrogen from a mixture of the two gases. |
| Litharge | |
| Precipitated carbonate of copper | |
| White lead | |
| Silver foil | Is unattacked if dry; under water it is quickly blackened. |

*Comments.*—Carbon oxysulphide, by reason of its ready change in presence of water into hydrogen sulphide and carbon dioxide, gives, in the main, the reactions of hydrogen sulphide, so that by the reagents usually employed for the detection of the latter gas these two sulphur compounds are not distinguishable. In fact, towards ammoniacal cadmium chloride solution, silver nitrate and palladium chloride, its reactions are characterized by somewhat greater promptness than in the case of hydrogen sulphide. It is to be noted that, should $H_2S$ and CSO occur in a gas mixture, the CSO would, by ordinary analytical methods, be mistaken for $H_2S$, and equal volumes of the two gases would yield the same weight of $Ag_2S$, CdS, CuS, etc.

The principal metallic sulphides as usually formed by $H_2S$ could be, in many cases, more rapidly produced by CSO; and, so far as I have been able to observe the reactions, there is little or no tendency to separation of free sulphur such as is common in precipitations by $H_2S$. The absorption of CSO in ammoniacal cadmium solution is so complete that on passing the gas through this solution none will escape unabsorbed to cause precipitation in a second solution. An analysis seemed desirable in the case of the silver compound obtained when CSO was passed through a solution of ammoniacal silver nitrate, as the precipitate appeared much more flocculent and of a more brownish color than ordinary precipitated silver sulphide.

Accordingly, determinations of silver and of sulphur were made with the following results:

| | FOUND. | | CALCULATED FOR $Ag_2S$. |
|---|---|---|---|
| | (1) | (2) | |
| Ag | 91.15 | 90.95 | 87.06 |
| S | 8.70 | 8.75 | 12.94 |
| | 99.85 | 99.70 | 100.00 |

Hence the compound consisted of silver sulphide, with a small quantity of silver thrown down by the carbon monoxide present in the gas.

Yellow mercuric oxide forms an excellent means of separation of the two gases, and, after the removal of the hydrogen sulphide by this reagent used in a dry state, the production of a precipitate in ammoniacal cadmium chloride solution would indicate that this cadmium sulphide has been caused by carbon oxysulphide.

The presence of a little carbon monoxide in the CSO made from KCNS and sulphuric acid is liable to mislead in the reaction towards palladium chloride, causing a black precipitate of palladium resembling the sulphide.

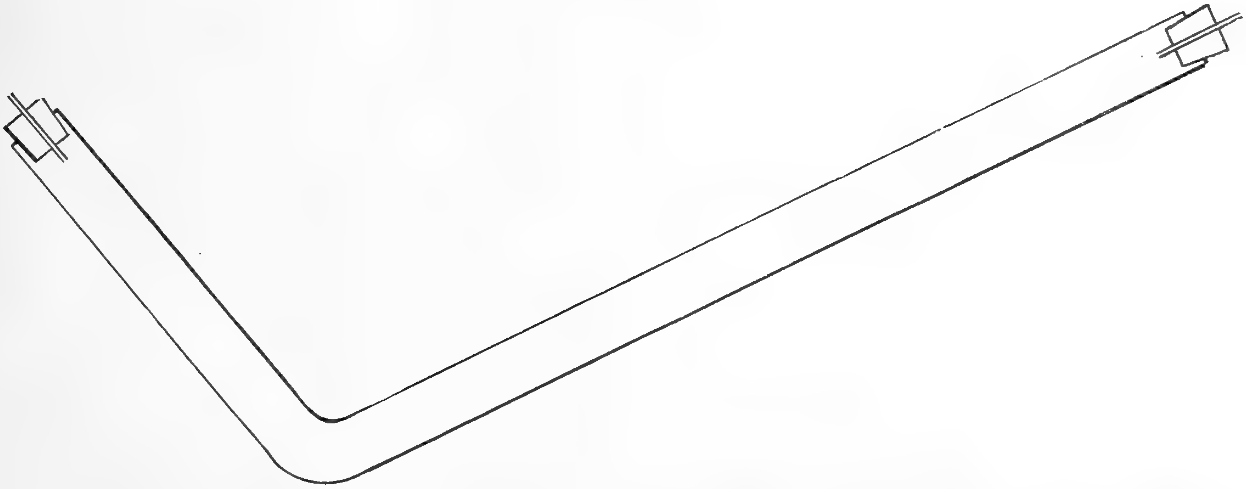
### METHYL HYDROSULPHIDE, $(CH_3)$ SH.

This gas may be produced by several typical reactions:

(1) When methyl chloride (bromide or iodide) is heated with KSH in alcoholic solution, the reaction being

$$CH_3Cl + KSH = KCl + CH_3SH.$$

Methyl chloride gas was conducted into a boiling alcoholic solution of KSH contained in a tube of the shape here shown.



The long limb of the tube (length, thirty inches) was connected with a reversed condenser and was heated over a small flame. The gas as it escaped was passed through a long glass tube containing cotton coated with red oxide of mercury, which absorbs any possible traces of hydrogen sulphide and some of the mercaptan. The gas was passed through broken ice. As the reaction above mentioned is rather incomplete, the gas contains much unaltered methyl chloride. The same is true when the bromide and iodide are used. Methyl chloride is the best suited to the purpose, since it may be conducted into the liquid as a *gas*. The iodide, being a very volatile liquid, is not easily added without danger of tumultuous boiling. Formation of difficultly soluble potassium chloride or iodide causes clogging and greatly interferes with the process, even when large delivery tubes are used.

(2) Methyl sodium sulphate and potassium hydrosulphide, on being brought together and warmed, yield the following reaction:

$$NaCH_3SO_4 + KHS = KNaSO_4 + CH_3SH.$$

The reaction may be carried out in aqueous solution by the very excellent method of Klason (*Ber.*, 1887, p. 3407).

Klason directs as follows:

800 gm. potassium hydroxide are dissolved in water; the solution is saturated by sulphuretted hydrogen. It is placed in a large flask and sodium methyl sulphate, made from 500 c.c. methyl alcohol, added in small portions. On gently warming, a mixture of the vapors of $(CH_3)_2S$ and $CH_3SH$ is evolved. The vapors are passed through an empty bottle and then into a second bottle containing soda solution, which should be cooled. The methyl hydrosulphide is completely absorbed by the soda forming $NaCH_3S$. The sodium mercaptide so produced is very stable. Methyl sulphide condenses to a liquid which floats on the soda solution, but does not combine with the soda. A separation is, therefore, easily effected. The methyl sulphide may be driven off by warming the bottle containing the soda solution, the $CH_3SNa$ being unaffected by the heat. The methyl sulphide may thus be used in vapor form to produce its reactions. After expulsion of the methyl sulphide, the soda solution may be placed in a flask and decomposed by dilute sulphuric acid and $CH_3SH$ then expelled as a gas. Some lead acetate is added to the solution in order to bind sulphuretted hydrogen during the decomposition of the sodium mercaptide by acid.

Klason advises a further purification; but, by the process described, the two sulphur compounds may be obtained of sufficient purity for the study of their reactions. Methyl hydrosulphide is a gas above 6° C. (Klason). It is remarkable for its penetrating odor, which adheres most tenaciously to all surfaces, glass not excepted, for months. All work with the gas should be done out of doors. It is somewhat soluble in water, to which it imparts its properties.

The compounds produced by the action of methyl hydrosulphide upon metallic oxides are the true mercaptides. Typical of these is the mercury mercaptide, which results as follows:

$$HgO + 2\,CH_3SH = (CH_3S)_2Hg + H_2O.$$

The yellow lead compound is $(CH_3S)_2Pb$. The copper compound is $(CH_3S)_2Cu$. The silver compound is (CHS)Ag (see Klason, *loc. cit.*, and Richter, *Org. Chem.*, trs. by Smith, p. 143). $CH_3SH$ also combines with metallic chlorides.

$$HgCl_2 + CH_3SH = CH_3SHgCl + HCl.$$

According to this reaction, numerous metallic compounds are formed. These compounds change more or less readily, on exposure to air, into methyl alcohol and metallic sulphide (Klason).

### *Reactions.*

The vapor was caused to bubble through various solutions with the following results:

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | Cinnamon-colored, flocculent precipitate in strong or weak solutions. Insoluble in hydrochloric acid, nitric acid, sulphuric acid, aquaregia, ammonia and caustic soda, in the cold or at 100°. Extremely delicate reaction. |
| Platinum chloride | Yellowish-brown, flocculent precipitate in dilute or concentrated solution. Insoluble in the strong acids and alkalies, and in this respect similar to the palladium compound. |
| Iridium chloride | Yellow precipitate, resembling in appearance the platinum compound. |
| Gold chloride | Light yellow, very voluminous precipitate, changing gradually to white as the passage of the gas is continued, and finally redissolving to a clear solution. |
| Mercuric chloride | White, flocculent precipitate. Darkens slightly on exposure to air and light. Extremely delicate reaction. |
| Copper sulphate | Straw-yellow precipitate, insoluble in ammonia. Darkens rapidly. Soluble in hydrochloric acid. The hydrochloric acid solution of the precipitate contains cuprous chloride. |
| Ammoniacal copper sulphate | Yellow precipitate like the preceding. Soluble in hydrochloric acid to cuprous salt. Rapidly darkens. |
| Cuprous chloride | White, flocculent precipitate, changing to crystalline needles. More stable than the preceding compound. |
| Silver nitrate | Yellow precipitate, resembling in appearance the copper compound. Insoluble in ammonia. Rapidly blackens. |

| | |
|---|---|
| Ammoniacal silver nitrate | Yellow precipitate, similar in appearance and properties to the preceding. |
| Ammoniacal cadmium chloride | White precipitate in flocculent masses, somewhat soluble in the reagent and in water. Permanent, if protected from the air. By oxidation is converted readily, in the cold, into yellow cadmium sulphide. |
| Arsenious chloride in dilute hydrochloric acid | The fluid grows milky from floating oil drops, which gradually collect as a very heavy oil at bottom. |
| Zinc sulphate in excess of caustic soda solution | Unchanged. |
| Potassium permanganate, 6 per cent. solution acidulated by hydrochloric acid. | Rapidly bleached. Becomes heated from the intensity of the reaction. No sulphuric acid is produced. |
| Lead acetate | Straw-yellow precipitate, insoluble in acids and alkalies. Rapidly blackens. |
| Potassium bichromate acidulated by hydrochloric acid. | Promptly reduced to green chromic chloride. No sulphuric acid is produced. |
| Bromine water | Rapidly bleached. No sulphuric acid is produced. |
| Mercurous nitrate | Grayish-black precipitate. |
| Bismuth nitrate | Slowly forming black precipitate. |
| Nickel hydroxide in water | Slowly blackens. |
| Ferric hydroxide in water | Unchanged. |
| Yellow oxide of mercury | Turns slowly gray and finally black. |
| Ferric chloride | Rapidly reduced to ferrous chloride. No sulphuric acid is formed and no sulphur liberated. |
| Potassium ferricyanide | Reduced to ferrocyanide. |
| Osmic acid | Rapidly blackened. |
| Potassium rutheniate | Extremely slow and incomplete reduction. |
| Hydrogen peroxide | No oxidation to sulphuric acid occurs. |
| Cerium dioxide in dilute sulphuric acid | Quickly bleached. |
| Litharge and white lead | Quickly changed, yielding a voluminous yellow powder. |
| Copper carbonate | The resulting mercaptide is similar in appearance to that obtained in the preceding reaction. The mercaptides of lead and copper are very stable. |
| Silver foil | Is not changed, dry or in water. After three months the silver appeared slightly darkened in color. |

*Comments.*—In the remarkable diversity of its reactions, methyl hydrosulphide probably excels every other known gas. The stability of many of its metallic compounds is often nearly as great as that of the corresponding sulphides. The reagents employed include many substances of high oxidizing power. It was not possible, however, to detect in any case a trace of sulphuric acid. Under the influence of oxidizing agents, the tendency of the mercaptans is to produce oxygen compounds, such as the sulphonic acids.

$$CH_3SH + O_3 = CH_3SO_3H.$$

Hence the failure to form sulphuric acid. The following experiment illustrates the remarkable stability of methyl hydrosulphide:

The gas was passed in slow stream through a glass combustion tube containing a fused mixture of sodium carbonate and potassium bichromate, but no sodium sulphate was produced. Moreover, the gas escaping from the tube possessed the characteristic odor of the mercaptan. The same experiment was tried with a mixture of sodium carbonate and sodium nitrate with a similar result. On account of its numerous reactions towards the various metallic salts, a separation of methyl hydrosulphide and sulphuretted hydrogen is a difficult matter. As it acts slowly and incompletely upon yellow mercuric oxide, this substance may be used to absorb sulphuretted hydrogen. Although methyl hydrosulphide attacks and combines with the mercuric oxide, sulphuretted hydrogen gradually expels it, the yellow color gradually changing to black, owing to the formation of sulphide of mercury. The yellow copper compound changes into copper sulphide. The same is true of the yellow compounds of lead and silver and the white cadmium compound. This change into sulphide is in every case promoted by exposure to air, especially in presence of ammonia. In an aqueous solution of methyl hydrosulphide containing neither acids nor alkalies, the various compounds are more stable.

The mercaptides are easily produced in many cases by the action of a solution of the mercaptan in water upon the oxides, hydroxides or carbonates of the metals, and when so formed they are easily preserved unchanged.

It is of importance to note that sulphuretted hydrogen expels methyl hydrosulphide from many of its metallic compounds. The reactions of $CH_3SH$ towards gold chloride and arsenious chloride are especially remarkable. In the former case the production of a precipitate, gradually changing from yellow to white and finally disappearing, distinguishes this gas from sulphuretted hydrogen. The formation of an oily liquid insoluble in water, in the case of arsenious chloride, also serves to distinguish between the two gases.

### METHYL SULPHIDE.

This compound may be prepared by the action of methyl iodide (or, preferably, methyl chloride) upon potassium sulphide in alcoholic solution. Gaseous methyl chloride may be led into an alcoholic solution of potassium sulphide contained in a flask heated over a water bath and connected with a reversed condenser. The vapor of methyl sulphide thus formed may be freed from sulphuretted hydrogen by oxide of mercury or by passage through warm soda solution.

In the process of Klason, already described, methyl sulphide is produced simultaneously with the hydrosulphide. The process yields, in fact, a larger proportion of the former than of the latter. It may be readily separated, as already stated, by means of soda solution, which absorbs and combines with the mercaptan but exerts no action upon the sulphide. On warming the soda solution, therefore, the sulphide, condensed and floating upon its surface, may be expelled in vapor form. In the following experiments methyl sulphide, prepared by the action of methyl chloride upon potassium sulphide and also by the method of Klason, was used.

Methyl sulphide is a colorless liquid, boiling at 37° C.

The compound formed by mercuric chloride with methyl sulphide is $(CH_3)_2SHgCl_2$. The yellow precipitate produced in platinum chloride solution is $PtS_2(CH_3)_4Cl_4$. On standing or on warming, the powder changes to a crystalline, isomeric form (for an important discussion of this and other alkyl sulphide compounds, see Enebuske, *J. Pr. Chem.* (2), XXXVIII, p. 358).

Bromine combines directly with methyl sulphide, yielding a crystallizable, volatile compound, $(CH_3)_2SBr_2$. Oxygen unites directly with methyl sulphide, yielding $(CH_3)_2SO$ and $(CH_3)_2SO_2$, and it appears, as already stated, to be impossible to oxidize the thioether to sulphuric acid by reagents in solution (see Richter, *Organic Chemistry*, trs. by Smith).

### *Reactions.*

In the following experiments the vapor was caused to pass into the various solutions.

| REAGENTS. | REACTIONS. |
|---|---|
| Palladium chloride | No change in highly dilute solution. In a 2 per cent. solution of palladium chloride, an orange-colored, pulverulent precipitate occurs, soluble on boiling. As the solution cools, the substance is redeposited in beautiful, orange-colored crystals. These crystals are apparently monoclinic and, although none were obtained sufficiently large for measurement, they resemble strongly the usual forms of selenite. |
| Platinum chloride | Precipitate of a lighter yellow color than the preceding. Somewhat soluble on heating, but less so than the palladium compound. The precipitate becomes distinctly crystalline on standing. |
| Gold chloride | Yellow precipitate, which becomes white and finally redissolves on continuing to pass the vapor through the solution. |
| Mercuric chloride | White precipitate. Very delicate reaction. When highly magnified the precipitate is seen to consist of transparent crystals, apparently monoclinic. |
| Copper sulphate | Unchanged. |
| Ammoniacal copper sulphate | Unchanged. |
| Silver nitrate | Turns brown, but little or no precipitation occurs. |
| Ammoniacal silver nitrate | Unchanged. |
| Cadmium chloride | Unchanged. |

| | |
|---|---|
| Ammoniacal cadmium chloride | Very slight precipitation, which dissolves in the reagent or in acid. |
| Arsenious chloride | Unchanged. |
| Potassium permanganate, acidulated by hydrochloric acid. | Rapidly bleached. No sulphuric acid is formed. |
| Lead acetate | Unchanged. |
| Bromine water | Rapidly bleached. On evaporation, a crystalline residue results. The substance is volatile in the cold. |
| Mercurous nitrate | Very dense, grayish-black precipitate. |
| Nickel hydroxide in water | Unchanged. |
| Ferric hydroxide in water | Unchanged. |
| Ferric chloride | Decided but incomplete reduction to ferrous chloride. |
| Yellow oxide of mercury in water | Unchanged. |
| Osmic acid | Rapidly reduced. |
| Potassium rutheniate | Very slowly and incompletely reduced. |
| Cuprous chloride | White crystalline precipitate, soluble in hydrochloric acid and reprecipitated by ammonia. Turns brown on washing with water. |
| Cupric chloride | Unchanged. |
| Iridium chloride | Yellow precipitate, resembling the platinum compound. |
| Hydrogen peroxide | No oxidation to sulphuric acid occurs. |
| Potassium ferricyanide | Very slow reduction to ferrocyanide. |
| Potassium bichromate acidulated with hydrochloric acid | Very slight reduction. No sulphuric acid is formed. |
| Cerium dioxide dissolved in sulphuric acid | Quickly bleached. |
| Precipitated carbonate of copper<br>Litharge<br>White lead<br>Lead chromate | These substances, tried separately in water, remained unchanged. |
| Silver foil in water | Unchanged. |

*Comments.*—The metallic compounds of methyl sulphide are, without exception, more soluble than those of methyl hydrosulphide. No insoluble compounds of methyl sulphide have yet been found. Towards oxidizing agents, methyl sulphide is as stable as methyl hydrosulphide. In no case was a trace of sulphuric acid produced, although the gas was subjected to the action of many very powerful oxidizing agents.

The gold chloride reaction is similar to that produced by methyl hydrosulphide.

Carbon oxysulphide is sharply distinguished from methyl sulphide and hydrosulphide by the ease with which it is oxidized to sulphuric acid by many oxidizing agents, such as bromine water or potassium permanganate in acid solution; moreover, the separation of sulphuretted hydrogen from carbon oxysulphide is easily effected, as already stated, by the yellow oxide of mercury.

Although not altogether satisfactory, the following plan may be used to recognize small quantities of methyl sulphide: The gas is passed through a small quantity of weak palladium chloride solution heated nearly to 100°. On spontaneous evaporation, the solution deposits monoclinic crystals easily recognized under the microscope. If the mercaptan compound appears (cinnamon-colored powder) the solution may be boiled. The methyl sulphide compound then goes into solution. The mercaptan compound is insoluble. On evaporating the filtrate, the methyl sulphide compound crystallizes in monoclinic prisms. If sulphuretted hydrogen and methyl hydrosulphide are suspected to occur, these two gases may be completely absorbed by caustic soda. The methyl sulphide is unabsorbed by soda, and by warming the soda solution it may be prevented from condensing upon the surface of the liquid. By using a solution of lead oxide in caustic soda, which absorbs sulphuretted hydrogen and methyl hydrosulphide, it is possible afterwards to expel the methyl hydrosulphide by cautious addition of dilute hydrochloric acid, the sulphuretted hydrogen being then held back by the lead as lead sulphide (Klason, *loc. cit.*).

Lastly, the terrible odor of the methyl hydrosulphide is sufficient for its identification under all circumstances.

## NITROGEN.

Although readily prepared by the absorption of oxygen from air by pyrogallol, the resulting nitrogen contains carbon monoxide, as shown by Tacke (*Archiv. f. d. Ges. Physiol.*, XXXVIII, p. 401). Ferrous sulphate in an excess of alkaline citrate solution is unsatisfactory as an absorbent for atmospheric oxygen on account of the extreme slowness of its action. I have found that ferrous chloride mixed with thick milk of lime acts more rapidly for the reason that, on agitating in a glass vessel, the pastry mass coats the walls and better exposure of the precipitated ferrous hydrate to the air is effected. The nitrogen used in the following experiments was prepared as described below.

Air was shaken with a mixture of pyrogallol and caustic soda solution. The resulting impure nitrogen was caused to pass slowly through a heated combustion tube filled partly with metallic copper (reduced by hydrogen from copper oxide) and partly with copper oxide.

Ledue (*Compt. Rend.*, V, CXIII, p. 71) has shown that copper used to remove oxygen from air should be made by the reduction of copper oxide at a low temperature, in order to avoid the formation of copper hydride and consequent contamination of the nitrogen by hydrogen. This impurity may, however, be removed by using some copper oxide in the heated tube. It may be stated that in a series of experiments, using pyrogallol and alkali in different proportions and in different degrees of concentration, it was not possible to obtain pure nitrogen. In every case the gas was found to exert a slight reducing action upon palladium chloride solution. The compounds of nitrogen result usually by indirect processes from other compounds. Additive reactions are rare.

Some interesting cases of direct union of nitrogen have been discovered by Merz (*Ber.*, 1891, p. 3942), who has shown that magnesium heated to redness in nitrogen produces a nitride. The nitride so formed is stable in dry air, but yields magnesium hydrate and ammonia in presence of moisture. So great is the affinity of magnesium for nitrogen that, on burning in moist air, the same compound results. The oxide formed always contains ammonia as a decomposition product of this nitride (Aslonoglow, *Chem. News*, LXII, p. 99). The combination of nitrogen and magnesium could only prove of interest as a gas reaction in case the formation of the compound is not interfered with by the presence of such gases as are not readily removable from a mixture. Sulphur and oxygen compounds would naturally be decomposed by magnesium.

In experiments with natural gas, as supplied to Allegheny, in October, 1892, it was found that magnesium heated to redness in a stream of the gas for one-half hour yielded a strong odor and the usual reactions characteristic of ammonia on moistening. The compound produced exhaled ammonia on exposure to air. Nitrogen also unites directly with lithium and potassium.

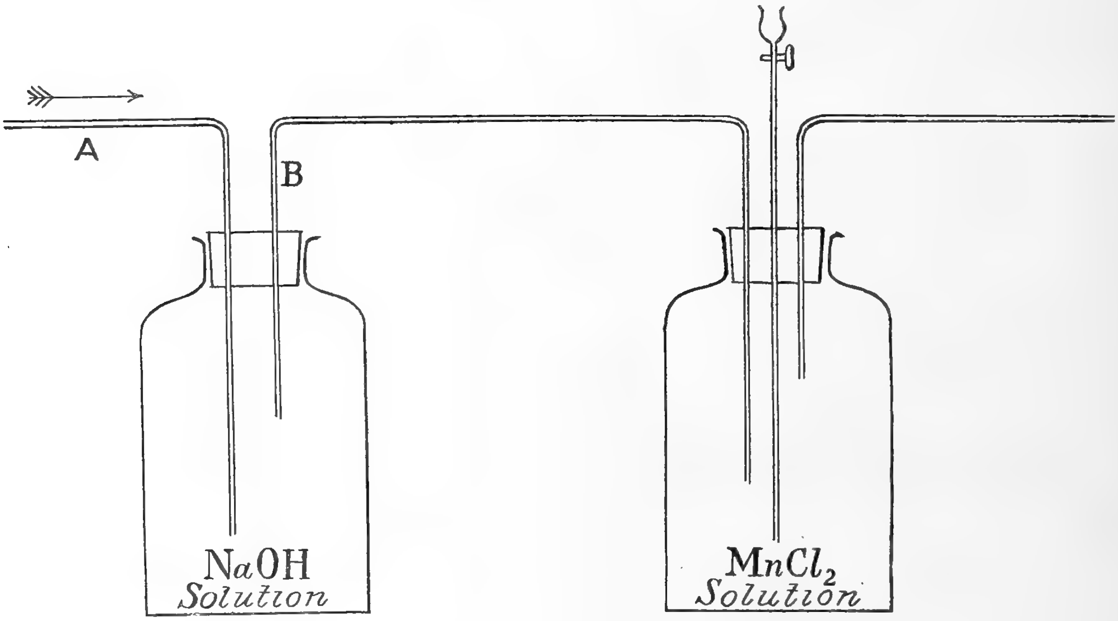
Ouvard (*Compt. Rend.*, CXII, p. 120) obtained a nitride of lithium containing 50.28 per cent. of nitrogen.

## OXYGEN.

### *Reactions.*

The presence of oxygen in very small quantities in a gas mixture is easily recognized by the change of color produced in a precipitate of ferrous ferrocyanide or manganous hydroxide, or in a solution of pyrogallol in soda, or indigo solution previously bleached by zinc dust. All of these substances absorb oxygen and at the same time undergo a change of color. The most sensitive of these is the mixture of pyrogallol and alkali. A very sensitive reagent for free oxygen is found in precipitated manganous hydroxide in water, which, by reason of very complete oxygen absorption, changes into $Mn_2O_3$, its color changing at the same time from white to brown. The following process is a modification of Winkler's method for the determination of dissolved oxygen in water (*Zeitschr. Ang. Chem.*, 1891, p. 105).

Two bottles of about two ounces capacity are connected as shown in the sketch. The gas stream enters by A and bubbles through soda solution and manganous chloride consecutively. After complete expulsion of air by the gas current, the tube B is pushed down so that some of the soda solution is forced over into the manganous chloride solution, causing a precipitation of manganous hydroxide. This precipitate remains white in the absence of oxygen. If oxygen be present, it gradually darkens in changing to $Mn_2O_3$. On adding now a little iodide of potassium solution and then sulphuric acid, by the tap funnel, the oxide of manganese redissolves, liberating iodine, recognizable by its color even when the most minute traces only of oxygen are present. The same apparatus can be used for pyrogallol and soda.



The method above described is very satisfactory in testing for oxygen in presence of paraffins, olefines, acetylene, allylene, carbon monoxide, carbon disulphide vapor. Sulphuretted hydrogen and carbon oxysulphide must be absorbed by ammoniacal cadmium chloride solution, or other suitable reagent, before the test can be applied. If an ammoniacal cadmium chloride solution is thus used, vapors of ammonia must be absorbed by dilute sulphuric acid before the reaction is tried. No difficulty occurs in applying the same reaction in testing a limited volume of gas. Instead of conducting the gas in a stream through the solutions, a eudiometer may be used. The reaction is, however, far less satisfactory, as the solutions are liable to hold atmospheric oxygen dissolved. By means of a standard hyposulphite solution the free iodine may be estimated; and, as 254 parts of iodine correspond to 16 parts of oxygen, the latter element is easily determined.

Pfordten (*Fres. Zeit.*, 1887, p. 74) proposes the use of chromous chloride in presence of sodium acetate for the quantitative determination (by absorption) of oxygen in a gas mixture. According to this author, the change from colorless to greenish blue renders the solution a suitable reagent for the recognition of oxygen. Very minute quantities of oxygen can be detected. The preparation of the reagent (reduction from chromic chloride by zinc in presence of hydrochloric acid) is effected in a Woulfe bottle, through which the gas is already passing, and the air thus removed previous to the test.

Fuming sulphuric acid is said to dissolve oxygen (B. Lean, *J. Ch. Soc.*, 1892, p. 880).

Nothing need be said here concerning the detection of oxygen when occurring in large quantities in a gas mixture.

The general study of gas reactions has not yet attracted the attention it deserves. The majority of articles bearing upon the subject have referred only incidentally to reactions by which a particular gas, or group of gases, may be recognized.

Every effort has been made to cite references to all published statements concerning reactions which I have detailed. It is probable, however, that many have been overlooked.

In conclusion, I have to express my thanks to Messrs. R. B. Carnahan, Gustav Miller and Henry Phillips, for assistance in the work, and especially to Mr. Henry T. Weed.

## III. SUBSTITUTION PRODUCTS OF THE ACTION OF CHLORINE UPON METHANE.

Natural gas was used in the following experiment. The gas was collected in June, 1888, from main conveying gas directly from Murraysville to Pittsburgh. A steel cylinder provided with thoroughly tested valves was filled from the gas main under a pressure of eighty pounds. An analysis of the gas showed it to have the following composition:

| | |
|---|---|
| Methane | 95.40 |
| Carbon dioxide | 0.20 |
| Carbon monoxide | 0. |
| Ethylene | 0. |
| Hydrogen | 0. |
| Oxygen | trace. |
| Nitrogen | 4.40 |
| | 100.00 |

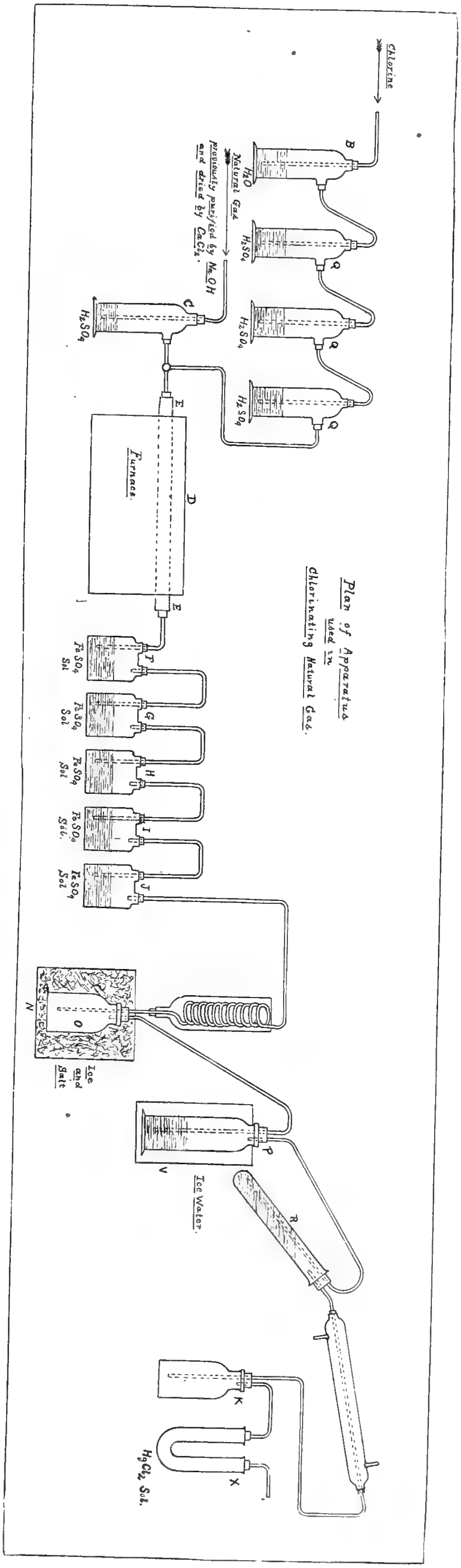
The following is an outline of the process of treatment:

Chlorine was generated in a large flask and washed in B before drying in Q. Natural gas was freed from carbon dioxide by caustic soda, and then dried by sulphuric acid. Q and C served at the same time to regulate the flow. E is a glass combustion tube which was filled with bone-black previously washed by hydrochloric acid. It was sought to produce the reaction:

$$CH_4 + 2\,Cl = CH_3Cl + HCl.$$

The furnace D was kept at the lowest possible temperature necessary to cause the color of the chlorine to disappear. After passing this tube, the gases were conducted through several bottles of ferrous chloride solution to remove any excess of chlorine, as well as hydrochloric acid. A reaction occurred at once in E. The chlorine disappeared. Too high a temperature caused a pale flame to appear in the combustion tube, which invariably led to a deposit of carbon. It was found necessary to maintain a very low temperature in the combustion tube. Slight condensation occurred in O of a clear liquid. Whether an excess of chlorine, or an insufficient quantity, or the theoretical quantity for the above reaction was used, there was formed continuously the tetrachloride of carbon, which collected in oily drops in F and G.

From experiments in using different proportions of chlorine and methane, employing higher and lower temperatures, and when sand or asbestos was substituted for the bone-black, and in using an empty combustion tube, I am led to the conclusion that the tendency is always to form methyl chloride and carbon tetrachloride;



Plan of Apparatus used in Chlorinating Natural Gas.

but that the intermediate products $CH_2Cl_2$ and $CHCl_3$ are only formed in relatively small quantity.

The manufacture of chloroform from natural gas, so far as these experiments indicate, is likely to prove of difficulty. The gas escaping from O has the odor of methyl chloride from methyl alcohol, is readily soluble in water and in alcohol, and burns with a green flame. The gas, after leaving P, passed into a solution of potassium hydrosulphide in R and then on into a solution of mercuric chloride in X. An immediate and copious precipitation occurred in X.

Methyl chloride from methyl alcohol, as is well known, is characterized by the property of forming a solid crystalline hydrate when conducted into icewater. The gas, prepared by the method above described, was passed through the bottle P containing broken ice while the ice was slowly melting, but no trace of a crystalline hydrate appeared.

It was not attempted to analyze the gas, for the reason that an analysis of a mixture of methyl chloride with some unaltered methane and traces of intermediate chlorides would lead to very uncertain results. The odor, the solubility in alcohol, the green color of the flame and the reaction with potassium hydrosulphide, all tend to show that it was methyl chloride. The failure to produce the crystalline hydrate with icewater I cannot explain.

It has long been considered a settled fact that only one methyl chloride is possible, Berthelot having shown (*Ann. Ch. Pharm.*, CV, p. 241) that when methyl chloride from methane and chlorine is treated with potash, saponification results with production of methyl alcohol, just as in the case of methyl chloride from woodspirit and hydrochloric acid.

Bæyer (*Ann. Ch. Pharm.*, CVII, p. 269, and *Watt's Dic.*, III, p. 987) states, that methyl chloride prepared from methyl alcohol and hydrochloric acid is different from the methyl chloride obtained by the action of chlorine on methane in the fact that the chloride from the latter source fails to form a crystalline hydrate when led into icewater, and that there are, therefore, two compounds isomeric, but not identical, having the formula $CH_3Cl$.

Roscoe and Schorlemmer (Vol. III, Pt. I, p. 203) explain the failure to form a crystalline hydrate by the methyl chloride from methane on the ground that other chlorinated substitution products occur with the methyl chloride. My experiments lead me to think that this does not satisfactorily explain the difference. $CH_2Cl_2$ and $CHCl_3$ do not occur except in traces in the gas which was produced, while $CCl_4$ was easily condensed in F and G (as it boils at 78° and cannot contaminate the methyl chloride).

The methyl chloride formed in the apparatus above described was caused to pass through a second combustion tube heated in a furnace, and through a side tube a stream of chlorine was passed directly into this second combustion tube. The methyl chloride supposed to have been formed by the action in the first furnace received, therefore, an additional quantity of chlorine before passing through the combustion tube in the second furnace. It seemed possible that in such a case the formation of higher chlorinated derivatives might be better controlled tnus:

$$CH_4 + 2\ Cl = CH_3Cl + HCl.$$

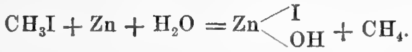
This equation represents the reaction probably occurring in the first combustion tube. The gases were then passed through water to remove hydrochloric acid. They were then dried by sulphuric acid and received the additional volume of chlorine, as above mentioned, before entering the second heated combustion tube. This reaction might then occur:

$$CH_3Cl + 2\ Cl = CH_2Cl_2 + HCl.$$

In the second tube the results were hardly different from those originally obtained. The methane tends constantly to produce methyl chloride or carbon tetrachloride, and there is little or no probability of obtaining intermediate products except in relatively very small proportions.

## IV. PREPARATION OF HALOGEN COMPOUNDS OF ALKYLS AND OLEFINES.

The alkyl iodides serve as the most convenient source for the preparation of the paraffins by the Gladstone and Tribe reaction, to which reference has already been frequently made, *e. g.:*



$$CH_3I + Zn + H_2O = Zn\langle{}^{I}_{OH} + CH_4.$$

The same compounds find application in forming the olefines by the action of KOH in alcoholic solution. Thus:

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

The olefine dibromides are of service in the preparation of olefines by means of zinc which abstracts the halogen, liberating the olefine. The acetylenes are most conveniently produced from the olefine dibromides, by the action of alcoholic potash, according to the reaction:

$$C_2H_4Br_2 + 2\ KOH = C_2H_4 + 2\ KBr + H_2O.$$

Hence, the selection of convenient methods in forming these iodine and bromine compounds has become a matter of much importance in the study of gas reactions.

The alkyl iodides are most easily formed by the action of iodine upon a mixture of red phosphorus and alcohol.

Chancel (*Ber.*, 1883, p. 2286 R, and *Bull. Soc. Chim.*, XXXIX, p. 648) has given a very convenient method for the preparation of propyl iodide and similar compounds. 127 gm. iodine, 60 gm. propyl alcohol and 10 gm. of red phosphorus are mixed in a flask, and, after the reaction, which at once sets in, has subsided, the flask is to be heated for an hour, connected with a reversed condenser. After cooling, the oily liquid is decanted, washed with soda solution and dried by calcium chloride. On distilling, nearly 90 per cent. of the theoretical yield is obtained.

This method gives very satisfactory results, and is applicable in the case of $CH_3I$, $C_2H_5I$, $C_3H_7I$, etc.

The process commonly recommended for the preparation of ethyl bromide by the addition of bromine to a mixture of ethyl alcohol and red phosphorus, yields a small and impure product and is difficult to control. Erlenmeyer (*Jahresb.*, 1878, p. 538) has given an excellent method for the preparation of ethyl bromide by the distillation of a mixture of potassium bromide, sulphuric acid and alcohol. Both of these processes yield a product largely contaminated by ether, which, although not removable by fractionation, may be completely separated from the ethyl bromide by digestion with sulphuric acid in the cold (as recommended by Riedel, *Ber.*, 1891, p. 105 R).

The olefine dibromides can be most easily prepared by the direct union of olefine with bromine. Meyer (*Ber.*, 1891, p. 4248) has, however, shown that in presence of iron (wire) as an "überträger," bromine attacks ethyl bromide, producing the reaction:

$$C_2H_5Br + 2\ Br = C_2H_4Br_2 + HBr.$$

This process, which requires heating in sealed tubes, in the case of ethyl bromide yields propylene dibromide in the cold from $C_3H_7Br$. The method is open to the objection that large volumes of HBr gas are necessarily evolved. Moisture wholly arrests the reaction.

Experiments tried in this laboratory with other metals (palladium, magnesium, aluminium) as "bromüberträger" and at varying temperatures, have failed to give satisfactory results in preparing ethylene dibromide. Not only heat, but pressure in sealed tubes is also necessary.

Allyl iodide, which has served as a more convenient material for the preparation of propylene than propyl iodide, was made by the action of iodine upon glycerine in the presence of both red and yellow phosphorus, by the excellent method described by Behal in *Ber.*, 1887, p. 693 R.

Iodides are to be preferred to bromides in all cases where KOH is used to produce a reaction, as KI is more soluble in alcohol than KBr. For this reason a larger quantity of KOH is necessary for a given reaction (formation of olefine from alkyl bromide) than in case of the iodine compound.

## V. COMPOSITION OF NATURAL GAS.

The gas used in the following trials was that supplied to Allegheny by the Allegheny Heating Company, and is the product of wells scattered over a considerable gas-producing area. It may be said to represent the average composition of an enormous volume of gas. No important differences have been observed during the period from 1886 to 1892 in the heating or illuminating power of the gas as supplied to the city, except that the odor of petroleum (*i. e.*, of higher paraffins) has been occasionally stronger.

Tests have also been made of gas from various localities in Pennsylvania, New York and Indiana, and Vancouver, British America, and also at Cleveland, O. In all cases where possible the tests were made at the wells. When this could not be done, it was necessary to use samples brought in glass vessels to the laboratory. In such cases, the samples were examined for oxygen before being subjected to the tests. As a leak in a sample vessel invariably causes an interchange of air and gas, so that air enters in proportion as an escape of gas occurs, much dependence is to be placed on the presence or absence of air in a gas sample as a criterion of its purity.

### HYDROGEN.

Hydrogen is almost always mentioned in the published analyses of natural gas I have made the following chemical tests: The natural gas, as supplied to Allegheny by the Allegheny Heating Company, was caused to flow through a solution of palladium chloride for periods varying from ten days to three months. Five hundred cubic feet have been used in a single experiment. Similar tests have been repeated at various times between January, 1886, and May, 1892; but in no case was a trace of precipitation observed in the palladium chloride solution. Natural gas was found likewise to be without action upon solutions of platinum chloride and ammoniacal silver nitrate. A stream of natural gas has been passed through *dry* pure palladium chloride. This extremely delicate test has failed to show the presence of hydrogen even in traces, although tried repeatedly during the period from January, 1886, until May, 1892. As already stated, the results of my study of gas reactions show that palladium chloride produces very different effects according as it is used dry or in solution. Palladium chloride *dry* is reduced promptly by dry hydrogen when the gas is used in a free state.

The same salt in solution is slowly and incompletely reduced by hydrogen, although it is rapidly reduced by olefines and carbon monoxide. Similar tests with palladium chloride, both dry and in solution, made at the wells, in the cases of all the localities mentioned in the table No. I, from 1 to 14, have led to similar results. Natural gas from Vancouver and from Kokomo, Ind., could not be tested at the wells. Tests made in the laboratory, of the samples received from those localities, gave the same negative results.

Another method of testing for hydrogen has been employed. As is well known, a jet of hydrogen is immediately ignited by platinum asbestos. Natural gas under similar conditions is not ignited, even when the gas jet and the platinum sponge are mounted in an oven kept at a temperature approaching 300°. In order to ascertain the effects of different proportions of hydrogen and natural gas, a gasometer containing the gas mixture to be tried was connected with a jet in form of a drawn-out glass tube, above which some platinum asbestos was fixed. The gas pressure could be so regulated as to produce a pointed flame one inch long. By momentarily shutting off the gas by pinching the hose, the flame could be extinguished, and the gas, being turned on again, played against the platinum asbestos. The length of the flame when the gas stream from the jet was ignited was therefore a measure of the gas flow. The gas was ignited by the platinum asbestos or not according as the proportion of hydrogen in the natural gas was greater or less. The ignition of the gas was also dependent upon the temperature of the oven in which the jet and the platinum asbestos were fixed.

Mixtures of hydrogen and natural gas produced glowing of the platinum and ignition of the gas at the following temperatures, when the experiment was made in a large iron oven whose temperature could be readily measured. The gas pressure was the same in all trials.

| PROPORTION OF HYDROGEN AND NATURAL GAS. | | TEMPERATURES OF THE OVEN AT WHICH THE GAS INFLAMES AS IT STRIKES THE PLATINUM ASBESTOS. |
|---|---|---|
| Natural gas | 95 | 40°–50° |
| Hydrogen | 5 | |
| Natural gas | 97.5 | 80°–90° |
| Hydrogen | 2.5 | |
| Natural gas | 99 | 180° |
| Hydrogen | 1 | |
| Natural gas | 99.5 | 210°–220° |
| Hydrogen | 0.5 | |
| Natural gas | 99.75 | 270° |
| Hydrogen | 0.25 | |
| Pure natural gas | | 270°–290° |

The observed temperatures naturally vary with the pressure, size of jet, etc., but trials with different pressures showed greater constancy than could be anticipated from a method so rough in appearance. The results corroborate those obtained by the more delicate tests. Experiments have also been tried with mixtures of air and natural gas which were exposed to palladium asbestos contained in glass tubes heated in the iron oven described under "Oxidation Temperatures of Hydrocarbons." It has been repeatedly shown that, under such conditions, moisture is only produced at temperatures approaching or higher than the melting point of cadmium iodide.

The absence of free hydrogen has interfered with the use of natural gas in gas engines. The prompt, sharp explosion of coal gas, so necessary for these motors, cannot be produced in the case of natural gas which requires a higher temperature for its ignition, and explodes with less suddenness owing to the absence of hydrogen.

The electrical devices for the igniting of coal-gas jets in dwellings by the spark of an induction coil, have not been so successful where natural gas is used, owing to the higher temperature of ignition of a gas consisting of paraffins and containing no hydrogen. In laboratories where natural gas is the fuel, chemists have experienced the inconvenience that Bunsen burners and blast lamps do not produce the high temperature easily obtained when coal gas is used. Ordinary glass combustion tubing cannot be softened by the employment of natural gas in a Berzelius blast lamp.

A coal-gas flame owes its steadiness and "stiffness" to the hydrogen which the gas contains. Natural-gas flames are much less steady and more easily extinguished by air currents.

During May, 1892, a change occurred in the composition of the natural gas supplied to Allegheny City. The gas since that time and up to November, 1892, has been found to contain hydrocarbons which reduce *dry* palladium chloride. These hydrocarbons are removed completely by digestion with fuming sulphuric acid, so that the gas after this treatment does not reduce palladium chloride. The nature of these hydrocarbons I have been unable yet to determine.

### OLEFINES.

Palladium chloride, iridium chloride, cerium dioxide in sulphuric acid, osmic acid, all remain unchanged by natural gas, cold or at 100°. Potassium permanganate is attacked with extreme slowness.

Bromine water has been repeatedly tried. The solution was in some cases cooled by ice to check evaporation of the bromine and in others the bromine was added slowly, drop by drop, to compensate for its evaporation. In no case were any oily drops produced. Prof. Sadtler, of Philadelphia, has in one instance obtained a considerable amount of heavy oil by the action of bromine on natural gas.

My experiments seem to prove the absence of ethylene, propylene, isobutylene and trimethylene from the gas supplied to Allegheny. The same is true of gas from the localities mentioned in the table from No. 1 to 17. Tests could not be made at the wells in the case of gas from Kokomo, Ind., and Vancouver, British Columbia; but samples brought to the laboratory gave similar results.

The very low illuminating power of natural gas of Western Pennsylvania is a further evidence of the absence of olefines which, as is well known, are remarkable for the brilliancy of the light which they produce. By the kindness of Mr. J. W. Patterson, gas inspector of Allegheny county, I am able to give the following data as to illuminating power.

The gas supplied to Pittsburgh by the mains of the Philadelphia Company, November 30, 1892, possessed an illuminating power equal to 10 84-100 candles per five cubic feet of gas burnt per hour (mean of ten determinations).

On the same date the illuminating power of the natural gas supplied by the People's Natural Gas and Pipeage Company was 10 77-100 candles.

Mr. Patterson's tests were made with a thirty-six-hole Argand burner, having a chimney seven inches long.

### ACETYLENE AND ALLYLENE.

Palladium chloride solution is unchanged, as already stated. Cerium dioxide, mercuric chloride, gold chloride, silver nitrate, ammoniacal cuprous chloride and osmic acid are all unchanged. Hence, in the gas I have tested, it may be said that no hydrocarbons of the acetylene series occurred.

I have found no reference to acetylenes in any published analyses to which I have had access.

### CARBONIC OXIDE.

Carbonic oxide is nearly always stated to occur in the published analyses of natural gas.

In my experiments, palladium chloride, gold chloride, silver nitrate in ammonia, iridium chloride, rhodium chloride, osmic acid, all used in solution, were unchanged.

Experiments have been made with Allegheny City natural gas in the following way: Gas has been caused to bubble for five weeks through ammoniacal cuprous chloride solution. This solution was then largely diluted with water and boiled. The gases expelled were collected and tested by palladium chloride solution; but no carbon monoxide was found. It is true that, since the absorption of carbon monoxide in cuprous chloride has been shown to be a case of mechanical solution rather than chemical union, and that the absorbed $CO$ can be expelled by a stream of other gases, the use of cuprous chloride for the absorption and recognition of carbon monoxide cannot be implicitly depended on. Still, the direct tests above named lead me to the conclusion that no carbon monoxide occurs in our natural gas.

### PARAFFINS.

That the lower paraffins occur in natural gas needs no proof. Methane is the chief constituent. Small quantities of higher paraffins are usually present.

### SULPHUR COMPOUNDS.

Pennsylvania natural gas does not contain recognizable quantities of either $COS$, $CH_3SH$ or $(CH_3)_2S$. Towards the western boundary of the State it is possible that minute traces of sulphuretted hydrogen occur. The quantities of all such compounds are far too small to allow of their being easily identified, even in the case of large volumes of gas. The extreme delicacy of the reaction of methyl mercaptan towards palladium chloride would render it possible to detect exceedingly minute quantities of this compound should it occur.

I have not had an opportunity to test the gas from the Western Ohio territory, which is said to contain sulphur compounds in considerable quantity.

### NITROGEN.

Natural gas, dried by calcium chloride and phosphorus pentoxide, was passed over strongly heated magnesium powder. The magnesium was partly converted into a nitride, easily recognized by its reaction towards moisture, yielding ammonia in considerable amount.

Repeated trials have been made of natural gas in the following way:

A measured volume of gas was passed over ignited oxide of copper contained in a porcelain tube, the entire apparatus having been previously filled with pure carbon dioxide, which was caused to flow in a continuous stream for several hours in order to expel all traces of air. The escaping gas was collected in a eudiometer over mercury and the carbon dioxide absorbed by soda. There was left invariably a residue of gas unabsorbed by the soda and having no action upon palladium chloride solution. This residual gas was evidently nitrogen (see Table of Analyses). In the gas found in an artesian boring at Middlesborough, England, nitrogen was found in large proportion (see Table of Analyses).

### OXYGEN.

By the use of pyrogallol and soda, and by the oxidation of manganous hydrate in water, I have frequently been able to detect traces of oxygen, although on other occasions no oxygen could be found. It has only been recognized when the gas had bubbled continuously for many hours or days through the reagent. It cannot be said that oxygen is a constant constituent, although it does unquestionably occur in much of natural gas in minute traces.

### CARBON DIOXIDE.

Carbon dioxide is present in all natural gas, as is easily proved by its action upon lime water.

### AMMONIA.

In the case of a gas well near Canonsburg, the following result was obtained: Gas was caused to bubble directly from the main at the well through water for several hours. On applying Nestler's reagent to the water, a feeble reaction was obtained. Ammonia was not found elsewhere in the trials I have made.

Mr. S. A. Ford, of the Edgar-Thompson Steel Works, reports a very interesting case where masses of solid ammonium carbonate were blown out from a gas well by the pressure of the gas.

Natural gas appears to consist chiefly of methane, with traces of higher hydrocarbons of the paraffin series. Nitrogen is probably always present, together with a little carbon dioxide. The absence of free hydrogen, of olefines and of carbon monoxide is, I believe, clearly shown in the case of the natural gas I have examined.

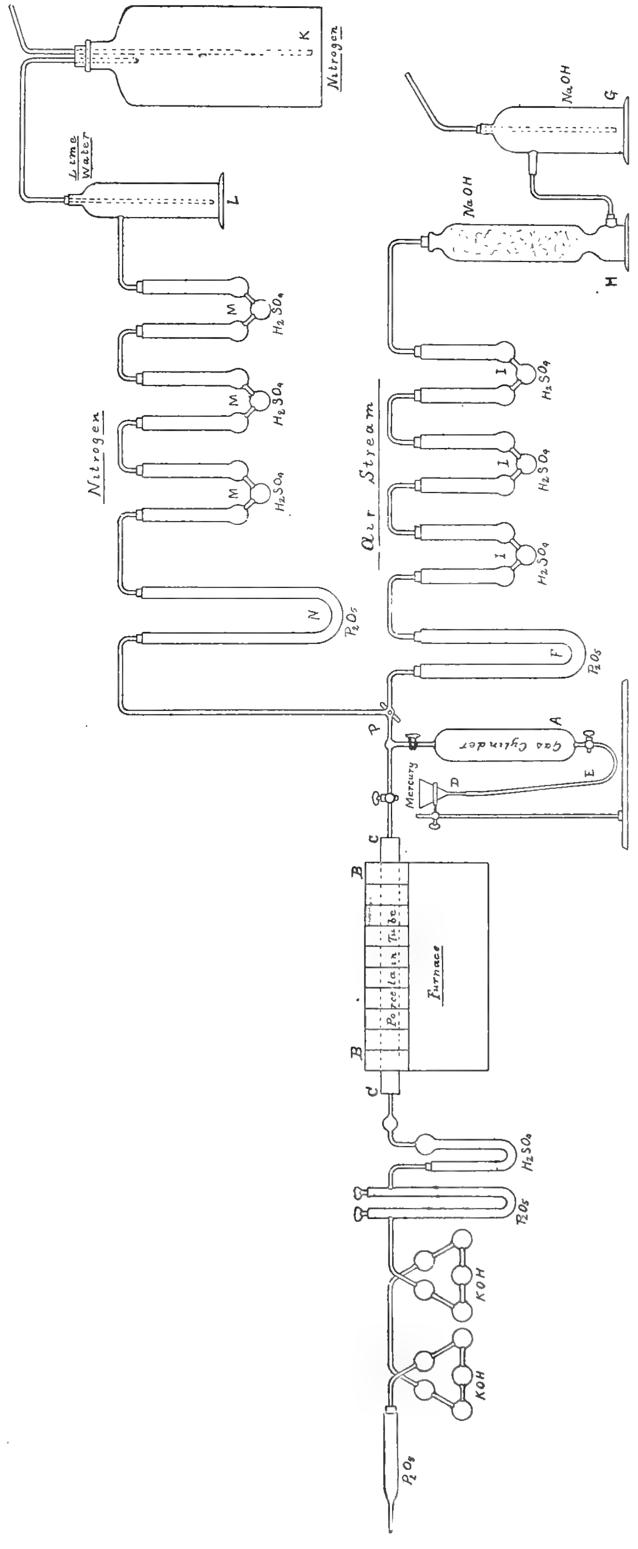
If natural gas as found in the wells of any one gas region is derived from one vast subterranean reservoir, approximate uniformity in composition should be looked for. It is often noticed, however, that gas from adjacent wells possesses a different odor.

A carbon dioxide determination was made in the case of samples of gas from six wells near Tarentum, Pa. These wells were situated nearly on a straight line less than one mile in length. The samples were all taken within an interval of three hours.

The determinations were made by a 7 per cent. soda solution in a eudiometer over mercury.

| WELL. | CARBON DIOXIDE. | WELL. | CARBON DIOXIDE. |
|---|---|---|---|
| No. 1 | 0.42 per cent. | No. 4 | 1.47 per cent. |
| " 2 | 1.25 " | " 5 | 1.28 " |
| " 3 | 0.25 " | " 6 | 1.28 " |

The differences in the proportion of carbon dioxide, a constituent determinable with great precision, would be difficult to explain if the gas flowing from these different wells is derived from one subterranean reservoir.



APPARATUS FOR QUANTITATIVE ANALYSIS OF NATURAL GAS.

## VI. QUANTITATIVE ANALYSIS OF NATURAL GAS.

It is not possible to determine the proportion of the individual paraffins in a gas mixture by the Bunsen method of explosion of oxygen unless it can be positively asserted that only two paraffins occur. This may be readily shown by an example. If a mixture of one volume each of marsh gas, ethane and propane is burnt, the volumes of oxygen required, carbon dioxide and steam produced will be as follows:

| | OXYGEN REQUIRED. | $CO_2$. | $H_2O$ VAPOR. |
|---|---|---|---|
| 1 vol. methane | 2 vols. | 1 vol. | 2 vols. |
| 1 " ethane | $3\frac{1}{2}$ " | 2 " | 3 " |
| 1 " propane | 5 " | 3 " | 4 " |
| | $10\frac{1}{2}$ " | 6 " | 9 " |

Three volumes of ethane require for combustion ten and one-half volumes of oxygen, and yield six volumes $CO_2$ and nine volumes of steam.

Hence a mixture of three gaseous paraffins could not be distinguished, in the case of a volumetric analysis, from the intermediate paraffin. Moreover, the heat of combustion of three volumes of the intermediate paraffin is almost exactly equal to that of a mixture of one volume each of the three.

From the fact last stated it follows that, as regards the calorific value of a mixture of paraffins, an exact determination of the character of the individual paraffins is not required.

A saving of time, the possibility of using a larger volume of gas, the avoidance of a volumetric determination of water vapor, are some of the advantages gained by a combustion over copper oxide.

The application of gravimetric methods for the examination of gas is not new. Winkler (*Handbook of Technical Gas Analysis*, p. 87) has described such a process for the analysis of mine gas.

*Description of Method.*—The process employed was, with some slight modifications, the same as described in the Annual Report of the Geological Survey of Pennsylvania for 1886.

Glass cylinders having stop-cocks at both ends, accurately calibrated by mercury and of 300–400 c.c. capacity, were filled with natural gas. Where possible, this was done at the well. Before filling with gas, finely drawn-out threads of glacial phosphoric acid were inserted through the stop-cock into the vessel. After twenty-four hours the gas sample could be considered dry.

Glacial phosphoric acid, on softening in the flame, may be readily drawn out like glass into rods of almost hairlike fineness. The quantity required was not sufficient to cause error in the gas measurements, inasmuch as the gas, as it flows from the wells, is in most instances remarkably dry.

The cylinder was then connected with a porcelain combustion tube, C, containing copper oxide. The general arrangement of the apparatus is shown in the accompanying sketch.

Before the communication was made between the tube C and the glass cylinder A, air was expelled from C by pure nitrogen dried in the tubes M. The combustion tube was intensely heated during the passage of the nitrogen.

After expulsion of air by nitrogen, the natural gas was caused to flow over the copper oxide previously heated for some time. The movement of the gas through the combustion tube was controlled by means of mercury, which flowed from the funnel D into the gas cylinder, and was so regulated that two hours were required for complete combustion.

Experiments showed that there is no danger of production of carbon monoxide or unsaturated hydrocarbons when the gas stream is slow.

After the gas had been expelled from the cylinder A, it was rinsed by lowering the mercury funnel so that nitrogen passed down into the cylinder, to be again driven out by raising the funnel.

After the gas had been fully burnt, air (purified by the lower system of drying tubes in the sketch) was passed through the apparatus till the nitrogen and moisture had been fully displaced and the process was then complete, the $CO_2$ and $H_2O$ being determined by weight. The method, as is seen, gives merely the proportions of carbon and hydrogen.

As the exact percentage of the paraffins in the gas mixture cannot be ascertained by analysis, an approximation alone is possible.

The composition by weight of some of the lower (gaseous) paraffins is as follows:

| PARAFFINS. | CARBON. | HYDROGEN. |
|---|---|---|
| Methane | 74.97 per cent. | 25.03 per cent. |
| Ethane | 79.96 " | 20.04 " |
| Propane | 81.78 " | 18.22 " |
| Butane | 82.72 " | 16.28 " |

In the following table, the calculated composition by weight of various mixtures of methane and ethane is given (the atomic weight of carbon being 11.97):

| MIXTURE OF | | | |
|---|---|---|---|
| METHANE. | ETHANE. | CARBON. | HYDROGEN. |
| 1 vol. | 1 vol. | 78.22 per cent. | 21.78 per cent. |
| 3 " | 2 " | 77.73 " | 22.27 " |
| 2 " | 1 " | 77.38 " | 22.62 " |

| | | | |
|---|---|---|---|
| 5 vols. | 2 vols. | 77.11 per cent. | 22.89 per cent. |
| 3 " | 1 " | 76.89 " | 23.11 " |
| 7 " | 2 " | 76.70 " | 23.30 " |
| 4 " | 1 " | 76.56 " | 23.44 " |
| 5 " | 1 " | 76.30 " | 23.70 " |
| 6 " | 1 " | 76.15 " | 23.86 " |
| 9 " | 1 " | 75.82 " | 24.18 " |

From a gravimetric analysis of natural gas, it is easy to determine the relative proportions by weight of carbon and hydrogen in unit volume, and from these the composition may be stated volumetrically in terms of ethane and methane, by the use of the preceding table, and with a fair approximation to the truth.

It is probable that minute quantities of propane and perhaps higher paraffins occur, but these cannot be identified. The nitrogen and carbon dioxide being determined, the volume of

$$CH_4 + C_2H_6 + C_3H_8 + \ldots\ldots$$

is obtained as a difference. The error involved in such a method may then be exactly defined as follows:

The hydrocarbons may consist of methane with traces of propane or of methane with ethane or butane, but the analysis will be stated volumetrically in terms of methane and ethane only.

As regards the question of fuel value, I have endeavored to show (see *Report of Geol. Survey of Penna. for* 1886) that the above method will give closely approximate results when certain factors relating to available heat of combustion of paraffins are used.

The gravimetric method affords at the same time a means of control, for it is not only true that in a given volume of a particular paraffin, or of a mixture of paraffins, the hydrogen and carbon will occur in definite quantity, but the ratio $\frac{C}{H}$ is a constant and will be greater as the proportion of higher to lower paraffins is greater.

These considerations will serve to show the limits of accuracy of the method.

Nitrogen was determined by passing a measured volume (100 c.c.) over ignited copper oxide contained in a porcelain tube, and then into a eudiometer containing soda solution. By means of a stream of carbon dioxide continued for several hours, the air was expelled from the apparatus previous to the combustion of the gas. In presence of large excess of carbon dioxide, combustion by copper oxide is greatly retarded, and the process must be conducted very slowly to effect complete oxidation.

Oxygen, as already stated, occurred in too small proportion to allow of a quantitative determination.

Carbon dioxide was determined by soda solution in a eudiometer over a mercury trough.

## ANALYSES OF NATURAL GAS.

| CONSTITUENTS. | FREEDONIA, N. Y. 1 | SHEFFIELD, WARREN CO., PA. 2 | KANE, M'KEAN CO., PA. 3 | WILCOX, M'KEAN CO., PA. 4 | SPEECHLY, NEAR OIL CITY, PA. 5 | LYONS RUN, MURRYSVILLE, PA. 6 | RACCOON CREEK, PA. 7 | HOUSTON, NEAR CANONSBURG, PA. 8 | MURRYSVILLE, PA. 9 | PITTSBURGH EXHIBIT'N GROUNDS, PA. 10 | CLEVELAND, O. 11 | CREIGHTON, PA. 12 | PAINTER & CO.'S WELL, PITTSBURGH, PA. 13 | BADEN, PA. 14 | KOKOMO, IND. 15 | ALLEGHENY CITY SALT WELL. 16 | VANCOUVER, BRITISH COLUMBIA. 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nitrogen | 9.54 | 9.06 | 9.79 | 9.41 | 4.51 | 2.02 | 9.91 | 15.30 | 4.40 | 7.30 | 6.30 | 0 | 0.70 | 12.32 | 6.00 | 7.10 | 6.30 |
| Carbon dioxide | 0.41 | 0.30 | 0.20 | 0.21 | 0.05 | 0.28 | trace | 0.44 | 0.20 | 0.52 | 0.20 | 3.64 | 0.40 | 0.41 | 0.40 | 0.30 | 0.14 |
| Hydrogen | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ammonia | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Oxygen | trace | trace | trace | trace | trace | trace | trace | trace | trace | trace | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sulphuretted hydrogen | 0 | 0 | 0 | 0 | 0 | 0 | trace | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Paraffins | 90.05 | 90.64 | 90.01 | 90.38 | 95.44 | 97.70 | 90.09 | 84.26 | 95.40 | 92.18 | 93.50 | 96.36 | 98.90 | 87.27 | 93.60 | 92.60 | 93.56 |
|  | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| The paraffins contained in these gas samples have the following composition by weight : |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Carbon | 78.14 | 76.69 | 76.77 | 76.52 | 77.11 | 74.96 | 76.42 | 76.68 | 75.15 | 75.40 | 76.40 | 75.80 | 75.51 | 76.48 | 75.40 | 75.44 | 75.23 |
| Hydrogen | 21.86 | 23.31 | 23.23 | 23.48 | 22.89 | 25.04 | 23.58 | 23.32 | 24.85 | 24.60 | 23.60 | 24.20 | 24.49 | 23.52 | 24.60 | 24.56 | 24.77 |

Nos. 1, 2, 3, 4, 5, 6, 7, 8, 14 are cited from *Report of Geol. Survey of Penna., 1886.*

Tests were made at the wells in all cases excepting Kokomo and Vancouver. In the case of these two localities samples were very carefully taken and forwarded by Mr. E. C. Somers (Kokomo) and Mr. C. F. Hutchings (Vancouver). (All the analyses were made by F. C. P.)

## VII. ORIGIN OF NATURAL GAS AND PETROLEUM.

Soon after the early discoveries of oil and gas in Pennsylvania, the geologists proposed a hypothesis to account for the origin of these remarkable substances.

Remains of the marine vegetation of the Devonian inland sea, as they were gradually buried under the later accumulations of sediment and exposed to gentle heat from below, underwent a slow process of destructive distillation. In this way, all the varieties of petroleum and natural gas were produced. This view, adopted from a purely geological standpoint, seemed so plausible that for a long period no other was thought of. Mr. J. F. Carll, of the Second Geological Survey of Pennsylvania, has discussed the hypothesis very exhaustively in his various official reports. If this view is correct, oil and gas are probably *stored products*, and are not being continuously generated at the present time.

Opposed to this view is the more strictly chemical hypothesis of Mendeléeff, who, in 1876, expressed his belief that petroleum and gas are of igneous origin.

On account of the high value assigned by astronomers for the mean density of the earth as compared with that of the surface rocks, it follows that the heavy metals are mainly accumulated at great depths where a temperature of fusion may be assumed. Many of these metals combine readily with carbon to form carbides. Iron, in form of a carbide, when exposed to steam at high temperatures, is rapidly oxidized, the hydrogen of the water then combining with the carbon set free and producing hydrocarbons.

Citing experiments of Cloez, who produced mixtures of hydrocarbon oils by the action of hydrochloric acid upon ferromanganese, Mendeléeff concluded that such reactions have occurred at great depths below the earth's surface by the contact of steam with incandescent metallic carbides.

"During the upheaval of mountain ranges, crevices would be formed at the peaks with openings upward, and at the foot of the mountains with openings downward. Thus there was opportunity for the water to penetrate to great depths and for the hydrocarbons to escape. The situation of naphtha at the foot of mountain chains is the chief argument in my hypothesis" (Mendeléeff, *Principles of Chemistry*, Vol. I, p. 365).

According to this view, oil and gas are being *continuously generated*, for there is no reason to suppose that the masses of metallic carbides in the earth's interior are exhausted; such, in fact, seems to be Mendeléeff's view.

Mendeléeff points especially to the absence of large quantities of nitrogen compounds in petroleum as an argument in favor of the hypothesis.

The objection has been urged against this hypothesis, that petroleum, if thus produced, should be abundant in the primary rocks from which it is usually absent. The originally heated condition of these rocks would have prevented the condensation of oil, however, and, although the vapors may have passed through the earlier rocks, there is no reason to expect that condensation should have occurred before reaching much higher strata.

While on geological grounds difficult to prove or disprove, it meets with one fatal objection. The composition of natural gas in Pennsylvania does not justify the supposition that superheated steam and carbon have been concerned in its formation. We should certainly look, in such a case, to find natural gas composed mainly of free hydrogen containing small quantities of paraffins, olefines and carbon monoxide. When it is considered that paraffins alone cannot under any known circumstances be produced from the oxidation of carbide of iron by steam, the hypothesis does not seem to be tenable.

It is true that varying conditions of temperature might have produced a great variety of hydrocarbons, but no evidence has yet been obtained that paraffins alone result from such a reaction. In an experiment made with ferromanganese and dilute sulphuric acid, the gas evolved was found to contain 6 per cent. of olefines.* It is further to be noticed that this hypothesis requires that water should take part in the process, yielding up its hydrogen, while, according to the older geological hypothesis, the water may have served mainly to cover and give protection from atmospheric oxidation, if it has been concerned at all in the reaction.

Water contains dissolved oxygen, and in descending to the iron carbides, must have given off its dissolved oxygen long before reaching the region at which actual formation of hydrocarbons could occur. Hence, on this hypothesis, oxygen should be found in natural gas in larger quantity than the chemical tests indicate. In fact in rocks of moderately high conducting power, a wide interval would exist between the depth at which water boils and the much greater depth at which water vapor could oxidize metallic iron in quantity. It is doubtful whether water could have traversed this interval so as to reach the latter depth at all.

Engler (*Ber.*, Vol. XXI, p. 1816, and Vol. XXII, p. 592) has published the results of interesting investigations upon the distillation products of menhaden fish oil. By conducting the distillation at a high pressure (25 atmospheres), this author produced a mixture of hydrocarbon oils from which a large number of normal

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* Experiments by F. C. P.

paraffins was obtained, compounds not found elsewhere in nature than in petroleum.

This has led to the revival of an older theory as to the origin of petroleum and gas, *i. e.*, that they have resulted from the distillation under pressure and at low temperatures of the accumulated remains of marine life buried under the sediments of the ancient Devonian seas.

Much has been written in support of the hypothesis of Engler, and it may be said to have gained very general acceptance in Europe.

Ochsenius (*Chem. Zeitung*, 1891, p. 936) has summarized many of the arguments usually adduced in support of the hypothesis.

This author says, "Concerning the origin of petroleum, there is now no doubt that, with a few exceptions, animal remains (mainly of marine life) have yielded the raw material."

Originally the opinion was held that it was derived from vegetable matters, because the accumulation of animal remains sufficient to account for its formation by any distillation process in the rocks could not be explained. Distillation of vegetable matters would, however, have left greater deposits of coal (as a residue in the Devonian rocks). But petroleum occurs in rocks of marine formation where coal is uncommon. Rocks in which plant remains are found do not contain bitumen (petroleum). If animal remains are associated with those of plants, then bitumen is usually found.

The objection urged against the hypothesis of Engler, that nitrogen does not occur in petroleum, is easily overcome by the fact that nitrogen of animal tissues tends finally to produce ammonia, and this in the case of petroleum may have been carried away in solution by water; hence, the absence of nitrogen compounds.

From Engler's experiments, it appears that animal fats are the chief source of petroleum.

It is true that fatty matters do not ordinarily sink in water, although Von Guembel, in the voyage of the *Gazelle*, found fat globules in dredgings from the bottom of the Atlantic Ocean, in water 15,000 feet deep.

Putrefactive changes would tend to yield considerable quantities of ammonia and carbon dioxide. These in presence of salt water would produce alkali bicarbonate and ammonium chloride. Hence, alkaline waters might be looked for in the neighborhood of petroleum. The petroleum at Pechelbronn is associated with water containing 0.5 per cent. of alkaline carbonate. (In Western Pennsylvania, many cases are known of water having a decided alkaline reaction in the neighborhood of gas wells. In the Murrysville gas territory, water of alkaline reaction was so abundant as to seriously interfere with gas development. Note by F. C. P.) Such alkaline waters are not known in archæan rocks, and are not, therefore, likely to be derived from greater depths than the rocks in which they are found.

Probably no cases can be cited where fatty tissues alone of buried animals have yielded oil or gas. The presence of strongly saline water is apparently needed.

Great differences occur in the chemical character of petroleum. Caucasian oils are mainly composed of olefines or substances related to the olefine group. The German oils are mixtures of paraffins and olefines, while the American are chiefly paraffins. Such differences may be attributed to the character of the rock in which the distillation has occurred. Sandstones would probably prove without action; while limestones, by reason of their basic character, would tend to strongly influence the products.

Such are some of the arguments of Ochsenius in favor of Engler's hypothesis.

If this view is accepted, it follows that the generation of petroleum and gas must be considered as a finished process, so far as all existing productive gas and oil regions are concerned.

Engler has analyzed the gas evolved when (1) menhaden oil and (2) when oleic acid are distilled under atmospheric pressure and under a pressure of 25 atmospheres.

| | MENHADEN OIL. | | OLEIC ACID. | |
|---|---|---|---|---|
| | 1 ATMOS. | 25 ATMOS. | 1 ATMOS. | 25 ATMOS. |
| Methane | 25.2 | 38.3 | 9.3 | 4.36 |
| Olefines | 11.4 | 7.8 | 12.5 | 2.9 |
| Carbon dioxide | 26.7 | 17.4 | 37.2 | 26.0 |
| Carbon monoxide | 34.9 | 34.5 | 38.6 | 25.5 |
| Incombustible residue | 1.8 | 2.0 | 2.4 | 2.0 |

(*Ber.*, 1889, p. 592).

The liquid distillates produced at the same time that these gases were evolved were rich in the normal paraffins and their isomers.

100 parts of menhaden oil yielded 8.9 parts of gas and 63 parts of liquid oils.

A strong argument in support of the Engler hypothesis is found in the fact that by distillation of fish oils, besides methane, several of the lower paraffins are produced in large quantity. Hydrocarbons of the paraffin series are not obtainable in such proportions by the distillation at high temperatures of other organic material under ordinary conditions.

It should be noted as a fact of much interest as regards the results of Engler's researches, that in the distillation at higher pressures the proportion of olefines contained in the gases evolved is considerably less. This is also true of carbon monoxide when oleic acid was distilled. It is to be regretted that Engler's experiments were not repeated at still higher pressures, in order to ascertain whether these same constituents of the evolved gases diminish progressively with increased pressure.

Engler was the first to show clearly that the problem of the origin of oil and gas must be studied from the chemical rather than the geological standpoint. The hypothesis advanced by this author has been very generally accepted.

Nevertheless, my examinations of natural gas have led me to doubt some of his conclusions, well founded as they seem. The most careful tests, carried on during a period of six years, have failed to show the presence of either olefines or carbon monoxide in the natural gas of Western Pennsylvania.

Some of the constituents of gas are soluble in water. This is notably the case with carbon dioxide, butane, hexane, etc. If ethylene and carbon monoxide have been produced even in much smaller proportion in the rocks than Engler finds in menhaden oil gas, these substances would now occur in the natural gas of Pennsylvania. Ethylene would give to the gas such illuminating power that there would be no occasion for the use of coal gas in any town in the Western Pennsylvania gas region. As a matter of fact, natural gas is almost useless as an illuminant, its light being equal to 5 to 11 candles per five feet of gas consumed per hour.

Mr. Robert McKinney, formerly gas inspector of Allegheny county, found as a mean of forty trials of natural gas supplied to Pittsburgh an illuminating power of 6.5 candles.

Mr. J. W. Patterson, the present gas inspector of the county, states that the illuminating power of natural gas as supplied to Pittsburgh in November, 1892, is a little less than 11 candles per five feet per hour. The reason for this is that natural gas, as found in Pennsylvania, does not contain olefines. If carbon monoxide occurred in gas, there would have been innumerable cases of poisoning among workmen at gas wells. It is common to find such leaks of gas about the majority of gas wells that no one could strike fire at a well without risk of fatal consequences. Although inhaling the escaping gas for much of a lifetime, a gas-well driller will usually maintain that no bad effects to health come from exposure to the gas. Air containing 0.2 per cent. of CO is known to produce dangerous effects upon health.

According to Wyss (*Zeit. Ang. Chem.*, 1888, p. 465), air containing 0.1 per cent. of water gas is poisonous to breathe.

It is hardly probable, moreover, that CO or $C_2H_4$ occurring in gas could have been absorbed or removed at low temperatures by any natural process in the rocks. Unlike carbon dioxide and ammonia, their slight solubility in water would preclude the supposition that they had been dissolved away. Muck (*Grundzüge und Ziele der Steinkohlenchemie*, 1881) cites analyses of fifty-seven samples of gas from coal mines and of gas occluded in coal. In only one case is carbon monoxide mentioned, but it is distinctly stated that its occurrence was not proved. Ethylene is mentioned in six cases, but Muck states that more recent analyses have failed to demonstrate its presence usually in gas from coal. The absence of hydrogen in all the analyses is especially noticeable. In the case of gases from the Caspian region, the presence of ethylene and carbon monoxide is to be anticipated, as, from all accounts, subterranean heat has been concerned in their production (see Table of Analyses).

Thomas (*Watt's Dic.*, Third Supp., p. 529) gives analyses of fourteen samples of gas occluded by coal and also of gas from blowers in coal mines in New South Wales. The analyses showed the presence of methane, nitrogen, carbon dioxide and oxygen; but no carbon monoxide, hydrogen or ethylene was found. Franke (*J. Pr. Chem.* (2), XXXVII, pp. 101, 113) gives analyses of mine gases, according to which only carbon dioxide and methane were found. Winkler (*Jahresb.*, 1882, p. 1063) found no hydrogen in nine samples of mine gas. Many similar statements might be cited, all tending to prove that hydrogen, ethylene and carbon monoxide do not occur in gases occluded in coal.

The occurrence of gas consisting of nearly pure nitrogen, such as that obtained at Middlesborough, England (see Table of Analyses), in a region therefore where gas similar to Pennsylvania natural gas might be looked for, may perhaps be explained by the action of subterranean water upon deposits of coal or bituminous shale. The dissolved air in such waters, by causing slow oxidation, might lead to the production of carbon dioxide and the consequent removal of oxygen from the

| CONSTITUENTS. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Carbon monoxide | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Carbon dioxide | 0.95 | 2.18 | 3.50 | 0 | 2.47 | 4.44 | 0 | 0.3 |
| Olefines | 4.11 | 3.26 | 4.26 | 0 | 0 | 0 | 0 | .... |
| Methane | 92.49 | 93.07 | 92.24 | 95.39 | 97.57 | 95.56 | 1.90 | .... |
| Hydrogen | 0.94 | 0.98 | 0 | 0 | 0 | 0 | 0 | .... |
| Nitrogen | 2.13 | 0.49 | .... | .... | .... | .... | 96.57 | 96.8 |
| Oxygen | .... | .... | .... | .... | .... | .... | 1.53 | 2.9 |
|  | 100.62 | 99.98 | 100.00 | .... | 100.04 | 100.00 | 100.00 | 100.00 |

Nos. 1, 2, 3, 4, 5 and 6, natural gas from the Caspian region. Communicated by letter from Mr. M. Belianing, of Nobel Bros., St. Petersburg. No. 4 is the result of a partial analysis. Nos. 7 and 8, gas obtained by deep borings at Middlesborough, England (Bedson, *J. Ch. Soc.*, 1888, p. 662).

water. The carbon dioxide produced would lessen the solubility of the water for nitrogen by causing the water to dissolve carbonate of lime, etc. Gentle heat from below would tend still further to the expulsion of the nitrogen, and thus a considerable but limited quantity of nitrogen might be obtained as a sudden outburst from a drill hole.

It may be said that varying conditions of temperature and pressure, and kind of rock, have modified the products, so that perhaps the carbon monoxide and ethylene resulting from a laboratory experiment have, in nature's workshop, given place to paraffins.

But, if the chemistry of the reaction supposed to occur is to be considered at all, the fact that distillation experiments have produced from fish oil certain bodies found in natural gas (paraffins), should not count more forcibly as geological evidence than the other fact, that such distillation yields bodies which are foreign to natural gas as usually found in Pennsylvania.

I have failed to find any data tending to show that organic matter can be subjected to destructive distillation in such a manner as not to yield carbon monoxide and considerable quantities of olefines, together with hydrocarbons of still less saturated character. As a rule, the acetylenes and benzol series appear. Engler's hypothesis involves the supposition that a process of distillation has occurred at moderately high temperatures and at pressures measured by great depth of rock strata. The carbon dioxide evolved in this destructive distillation must have come continuously into contact with the vast quantities of carbon, which in its various stages of transformation from vegetable tissue to anthracite is so widely distributed throughout the rocks. The reaction $CO_2 + C = 2\ CO$, which proceeds rapidly at a strong heat and also slowly at lower temperatures, would then probably have occurred, wherever the temperature was sufficiently high.

Prolonged contact of carbon dioxide with the carbonaceous residue of the distillation would perhaps be sufficient to increase considerably the final yield of carbon monoxide.

According to I. L. Bell (*Chemical Principles of the Manufacture of Iron and Steel*, p. 101) the reduction of carbon dioxide to carbon monoxide by carbon in the form of soft coke begins at 427° C.

This is about the temperature at which Engler's distillation experiments were conducted (360°–420° C.).

Engler has shown that distillation of animal fats at very high pressure (25 atmospheres) may yield gas containing less of carbon monoxide and olefines than when the process is conducted under atmospheric pressure. No data are at hand as to results at still higher pressure. If it is conceded that the proportion of carbon monoxide and ethylene in the gas evolved during destructive distillation decreases progressively with increase of pressure, and that these two constituents vanish altogether at sufficiently high pressures, it would still seem necessary to suppose that the pressure must have been at least twice as great when the process occurred in the rocks, as in the case of Engler's experiments.

Taking the specific gravity of the rocks to be about 2½, it may be assumed that twelve feet of rock strata represent a pressure of 1 atmosphere, six hundred feet of solid rock would then be required to produce a pressure of 50 atmospheres. This would be considerably less than the depth of the same quantity of rock material in the form of loose sediment, before its consolidation. No case can be cited in recent times where sediment six hundred feet deep has been so suddenly accumulated as to bury unchanged the vast quantities of animal remains necessary to account for the production of oil and gas upon Engler's hypothesis, that oil and gas have resulted from the action of pressure and moderate heat upon animal matters.

There is probably no reason to suppose that the gaseous olefines have, under the influence of pressure, given place to others of higher boiling point, by a process of polymerization. Should the possibility of such a change be proved, the absence of olefines from natural gas and their presence in petroleum might be explained. The possibility of secondary reactions among the constituents of a complex gas mixture at high temperatures and under pressure, adds difficulty to the problem, and caution is needed to avoid the error of overestimating the importance of any given reaction.

It is generally true, however, that under such conditions secondary changes are probable, and that unsaturated compounds—olefines, acetylenes, carbon monoxide—are likely to result, especially when water vapor and carbon dioxide are present.

It is a well-known fact, that when petroleum is distilled, considerable quantities of unsaturated hydrocarbons are produced which did not exist in the original crude oil. This is shown by the bromine absorption of the different products. The process of "cracking" or breaking up by heat of the hydrocarbons in petroleum into simpler and less saturated compounds, is familiar to all oil refiners. Chemically speaking, "cracking" means the production of unsaturated hydrocarbons.

The fact that Engler has, in his extremely interesting and important researches, produced by distillation of animal matters, so great a variety of paraffins, constitutes by far the strongest argument in favor of his hypothesis.

Sorge, in an article which has been reproduced in numerous journals (*J. Ch. Soc.*, 1888, p. 31, abstract), has stated, that a strong resemblance exists between Pennsylvania natural gas and gas manufactured from Westphalian coal. Similarity in composition between natural gas and coal gas would greatly simplify the problem of origin, and the fact of such similarity would prove of great interest. In this connection, the following analysis of gas from Westphalian coal, carried out in the laboratory of the Westphalian Berggewerkschaftskasse in Bochum, will be of interest. I am indebted to Mr. Bergassessor E. Krabler, of Bochum, for the figures which he has kindly communicated by letter.

| | 1. | 2. |
|---|---|---|
| Hydrocarbons, $C_xH_y$ | 5 | 4 |
| Methane | 45 | 35 |
| Hydrogen | 40 | 50 |
| CO | 5 | 5 |
| $CO_2$ | 1 | 3 |
| Nitrogen | 4 | 3 |

The large percentage of hydrogen and the proportion of CO in this gas illustrate at once the results of high temperature in the production of the coal gas, but a similarity between this coal gas and natural gas can hardly be said to exist.

When vegetable remains are buried under water, as is well known, decomposition occurs, yielding gas in considerable quantity.

Tappeiner (*Ber.*, 1883, p. 1734) has studied the products of this change very exhaustively.

Pure cellulose (filter paper) was found, under the influence of a microbe which was supplied with nutritive fluids, to dissolve in water, yielding gas mixtures of two different types.

| | UNDER WATER OF NEUTRAL REACTION. | | UNDER SLIGHTLY ALKALINE WATER. |
|---|---|---|---|
| | AT BEGINNING. | AT END. | |
| Carbon dioxide<br>Hydrogen sulphide | 85.48 per cent. | 76.98 per cent. | 55.39 per cent. |
| Hydrogen | 0.0 " | 0.0 " | 42.71 " |
| Methane | 11.86 " | 23.01 " | 0.0 " |
| Nitrogen | 2.73 " | 0.0 " | 1.90 " |

From these experiments it appears that, by the action of a microbe, either methane and carbon dioxide (neutral fluid), or hydrogen and carbon dioxide (alkaline fluid) may result. Hoppeseyler (*Ber.*, 1883, p. 122) found that gas evolved in the decay of cellulose under the influence of a microbe (marsh-gas fermentation) contained:

| | |
|---|---|
| Carbon dioxide | 50 per cent. |
| Methane | 45 " |
| Hydrogen | 4 " |

Popoff finds in a gas from decaying vegetable matters:

| | |
|---|---|
| Marsh gas | 68 56 per cent. |
| Carbon dioxide | 31.44 " |

Berthelot states that hydrogen is produced in the vinous fermentation of mannite. In very careful experiments which I have tried I have failed to find hydrogen in the gas evolved during the fermentation of 200 gms. of sugar. Chemical changes of this type are not likely to be of importance, however, as regards the hydrogen question.

### GASES FROM SEA WEEDS.

The following experiments were tried in order to study the nature of the gases evolved in the decay of sea weeds:

A quantity of a large fucus kind from Santa Barbara, Cal., was used. 50 gms. of the air-dried plant were soaked in water and then introduced into a flask filled with water, which had been previously boiled (in order to expel air) and cooled. The flask was connected with a belljar over a mercury trough. After setting up the apparatus, no gas appeared until the third day; then a strong evolution of gas began and continued in slowly diminishing quantity for ten days, when the process ceased. In all, 803 c.c. of gas were collected. Analyses were made (1) of the first portion of 300 c.c., (2) of a second portion of 300 c c., and (3) of the last portion of 203 c.c. The results are tabulated below.

| | FIRST PORTION. | SECOND PORTION. | THIRD PORTION. |
|---|---|---|---|
| Carbon dioxide | 18.23 per cent. | 32.47 per cent. | 53.44 per cent. |
| Carbon monoxide | 0 " | 0 " | 0 " |
| Ethylene | 0 " | 0 " | 0 " |
| Methane | 0.30 " | 0.28 " | 0.08 " |
| Hydrogen | 62.24 " | 48.97 " | 42.02 " |
| Nitrogen | 19.23 " | 18.28 " | 4.46 " |
| | 100.00 | 100.00 | 100.00 |

Carbon dioxide was determined by soda solution over mercury; hydrogen by palladium asbestos, using a Hempel apparatus. The absence of CO and $C_2H_4$ was proved by palladium chloride solution. Methane was determined by combustion with air, using a red-hot platinum tube. The carbon dioxide produced in the combustion was absorbed by baryta solution of known strength, and the excess of baryta determined by standard oxalic acid. The following facts are of especial interest:

1. The carbon dioxide increases towards the end of the decay. 2. The hydrogen steadily diminishes. 3. Methane occurs only in traces. 4. Nitrogen occurs in

such considerable quantity as to render it probable that this gas is set free in the process of decay.

The same apparatus was kept in position for two and a half years after the above experiments were finished. During that time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 c.c. of gas collected. This was found to consist of methane.

I have examined the gases produced in swampy ground in many different places. Samples were taken from streams having muddy bottoms and in which vegetable matter had collected. Samples of gas have also been taken from salt marshes on the coast of Maine. Gas has also been collected from the very deep accumulations of mud and decaying vegetable remains found in some parts of Lake Chautauqua. The general result of examinations of these gas samples may be stated to the effect that the gas occurring in shallow swamps and streams consists of methane, carbon dioxide and nitrogen. In some of the much deeper swamp waters, where masses of vegetable débris of greater thickness are found (as in Lake Chautauqua), hydrogen occurs in very small quantity. Great difficulty is experienced in taking samples of gas from localities of the latter type. Tappeiner observes that the marsh-gas fermentation is very probably a very important source of methane in nature.

The fact that buried vegetable matters may, after a brief period of rapid gas evolution, pass into a condition of extremely slow decay, adds greater force to the original theory of petroleum and gas. The occurrence of so large a proportion of free hydrogen among the gases evolved by vegetation in process of decay is a matter of great interest, as it suggests the existence of an important source of hydrogen wherever deeply submerged plant remains occur. Frankland (*J. Ch. Soc.*, 1883, p. 295) found that grass left to decay under water (air being excluded) evolved gas in three days of the following composition:

| | | |
|---|---|---|
| Carbon dioxide | 84.63 | per cent. |
| Oxygen | 0.13 | " |
| Hydrogen | 6.90 | " |
| Other combustible gases | 2.51 | " |
| Nitrogen | 5.83 | " |

Vegetable tissue, after the somewhat sudden and tumultuous evolution of gas, seems to be capable of relapsing into an extremely slow and long continued process of decay. After the first decomposition, such remains might become accumulated and buried deeply under sediments before the tissues are materially altered. The generation of gas might then proceed in the cold. It seems hardly possible to ignore this probable source of natural gas in discussing any theory as to its origin, especially when it is considered that no other process in nature has been found to yield a gas at all similar in composition to that found in the rocks.

Of the three hypotheses which have been proposed to account for the production of oil and gas, two are open to a serious objection.

The chemical changes supposed by Engler to have been the cause, would probably yield gas different in composition from the natural gas now being obtained in such large quantity in Western Pennsylvania, and if the gas originally contained ethylene and carbon monoxide it is not easy to explain their complete disappearance in the natural gas I have examined from wells scattered over so large a region.

The hypothesis of Mendeléeff would be much more difficult to reconcile with the facts as regards composition. The total absence of hydrogen could not be easily explained. The only process in nature which is known to yield gas similar in its constituents to natural gas is that which occurs in swamps and decaying masses of submerged vegetable remains.

The important fact that the solid plant tissues may be preserved for long periods after the preliminary gas evolution has ceased shows that the remains are likely to become slowly buried, to undergo the "fermentation" changes leading to the production of methane.

Animal tissues can suffer no such arrest of decomposition. Decay once set in is carried rapidly onward to complete destruction without intermission. The contrast between the conditions in which animal and plant remains occur in the rocks seems to justify this statement.

If chemical evidence shall count in the discussion, it is difficult to find a more satisfactory explanation than the older hypotheses which the geologists advanced, although in their treatment of the subject the strictly chemical arguments were neglected.

# TRANSACTIONS

OF THE

# AMERICAN PHILOSOPHICAL SOCIETY,

HELD AT PHILADELPHIA,

## FOR PROMOTING USEFUL KNOWLEDGE.

VOL. XVII.—NEW SERIES.

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PART I.

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Philadelphia:
PUBLISHED BY THE SOCIETY,
AND FOR SALE BY
THE AMERICAN PHILOSOPHICAL SOCIETY, PHILADELPHIA
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# EXTRACT FROM THE LAWS.

## CHAPTER XII.

### OF THE MAGELLANIC FUND.

SECTION 1. John Hyacinth de Magellan, in London, having in the year 1786 offered to the Society, as a donation, the sum of two hundred guineas, to be by them vested in a secure and permanent fund, to the end that the interest arising therefrom should be annually disposed of in premiums, to be adjudged by them to the author of the best discovery, or most useful invention, relating to Navigation, Astronomy, or Natural Philosophy (mere natural history only excepted); and the Society having accepted of the above donation, they hereby publish the conditions, prescribed by the donor and agreed to by the Society, upon which the said annual premiums will be awarded.

### CONDITIONS OF THE MAGELLANIC PREMIUM.

1. The candidate shall send his discovery, invention or improvement, addressed to the President, or one of the Vice-Presidents of the Society, free of postage or other charges; and shall distinguish his performance by some motto, device, or other signature, at his pleasure. Together with his discovery, invention or improvement, he shall also send a sealed letter containing the same motto, device or signature, and subscribed with the real name and place of residence of the author.

2. Persons of any nation, sect or denomination whatever, shall be admitted as candidates for this premium.

3. No discovery, invention or improvement shall be entitled to this premium, which hath been already published, or for which the author hath been publicly rewarded elsewhere.

4. The candidate shall communicate his discovery, invention or improvement, either in the English, French, German or Latin language.

5. All such communications shall be publicly read or exhibited to the Society at some stated meeting, not less than one month previous to the day of adjudication, and shall at all times be open to the inspection of such members as shall desire it. But no member shall carry home with him the communication, description, or model except the officer to whom it shall be entrusted; nor shall such officer part with the same out of his custody without a special order of the Society for that purpose.

6. The Society, having previously referred the several communications from candidates for the premium, then depending, to the consideration of the twelve counselors and other officers of the Society, and having received their report thereon, shall, at one of their stated meetings in the month of December, annually, after the expiration of this current year (of the time and place, together with the particular occasion of which meeting due notice shall be previously given, by public advertisement) proceed to final adjudication of the said premium: and, after due consideration had, a vote shall first be taken on this question, viz.: Whether any of the communications then under inspection be worthy of the proposed premium? If this question be determined in the negative, the whole business shall be deferred till another year; but if in the affirmative, the Society shall proceed to determine by ballot, given by the members at

large, the discovery, invention or improvement most useful and worthy; and that discovery, invention or improvement which shall be found to have a majority of concurring votes in its favor shall be successful; and then, and not till then, the sealed letter accompanying the crowned performance shall be opened, and the name of the author announced as the person entitled to the said premium.

7. No member of the Society who is a candidate for the premium then depending, or who hath not previously declared to the Society, that he has considered and weighed according to the best of his judgment, the comparative merits of the several claims then under consideration, shall sit in judgment, or give his vote in awarding the said premium.

8. A full account of the crowned subject shall be published by the Society, as soon as may be after the adjudication, either in a separate publication, or in the next succeeding volume of their Transactions, or in both.

9. The unsuccessful performances shall remain under consideration, and their authors be considered as candidates for the premium for five years next succeeding the time of their presentment; except such performances as their authors may, in the meantime, think fit to withdraw. And the Society shall annually publish an abstract of the titles, object, or subject matter of the communications, so under consideration; such only excepted as the Society shall think not worthy of public notice.

10. The letters containing the names of authors whose performances shall be rejected, or which shall be found unsuccessful after a trial of five years, shall be burnt before the Society, without breaking the seals.

11. In case there should be a failure, in any year, of any communication worthy of the proposed premium, there will then be two premiums to be awarded the next year. But no accumulation of premiums shall entitle the author to more than one premium for any one discovery, invention or improvement.

12. The premium shall consist of an oval plate of solid standard gold of the value of ten guineas. On one side thereof shall be neatly engraved a short Latin motto suited to the occasion, together with the words: "The Premium of John Hyacinth de Magellan, of London, established in the year 1786;" and on the other side of the plate shall be engraved these words: "Awarded by the A. P. S. for the discovery of ——— A.D. ——." And the seal of the Society shall be annexed to the medal by a ribbon passing through a small hole at the lower edge thereof.

SECTION 2. The Magellanic fund of two hundred guineas shall be considered as ten hundred and fifty dollars, and shall be invested separately from the other funds belonging to or under the care of the Society, and a separate and distinct account of it shall be kept by the treasurer.

The said fund shall be credited with the sum of one hundred dollars, to represent the two premiums for which the Society is now liable.

The treasurer shall credit the said fund with the interest received on the investment thereof, and, if any surplus of said interest shall remain after providing for the premiums which may then be demandable, said surplus shall be used by the Society for making publication of the terms of the said premium, and for such purposes as may be authorized by its charter and laws.

The treasurer shall, at the first stated meeting of the Society in the month of December annually, make a report of the state of said fund and of the investment thereof.

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**Part** II.—*The Tribute Roll. By Henry Phillips, Jr.*
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# EXTRACT FROM THE LAWS.

## THE HENRY M. PHILLIPS' PRIZE ESSAY FUND.

Miss Emily Phillips, of Philadelphia, a sister of Hon. Henry M. Phillips, deceased, presented to the American Philosophical Society, held at Philadelphia for Promoting Useful Knowledge, on October 5, 1888, the sum of five thousand dollars for the establishment and endowment of a Prize Fund, in memory of her deceased brother, who was an honored member of the Society. The Society, at a stated meeting, held October 5, 1888, accepted the gift and agreed to make suitable rules and regulations to carry out the wishes of the donor, and to discharge the duties confided to it. In furtherance whereof, the following rules and regulations were adopted by the Society at a stated meeting held on the seventh day of December, A.D. 1888.

*First.* The Prize Endowment Fund shall be called the "Henry M. Phillips' Prize Essay Fund."

*Second.* The money constituting the Endowment Fund, viz., five thousand dollars, shall be invested by the Society in such securities as may be recognized by the laws of Pennsylvania, as proper for the investment of trust funds, and the evidences of such investment shall be made in the name of the Society as Trustee of the Henry M. Phillips' Prize Essay Fund.

*Third.* The income arising from such investment shall be appropriated as follows:

(*a*) To making public advertisement of the prize and the sum or amount in United States gold coin, and the terms on which it shall be awarded.

(*b*) To the payment of such prize or prizes as may from time to time be awarded by the Society for the best essay of real merit on the Science and Philosophy of Jurisprudence, and to the preparation of the certificate to be granted to the author of any successful essay.

*Fourth.* Competitors for the prize shall affix to their essays some motto or name (not the proper name of the author, however), and when the essay is forwarded to the Society, it shall be accompanied by a sealed envelope containing within the proper name of the author, and, on the outside thereof, the motto or name adopted for the essay.

*Fifth.* At a stated meeting of the Society, in pursuance of the advertisement, all essays received up to that time shall be referred to a Committee of Judges, to consist of five persons, who shall be selected by the Society from nomination of ten persons made by the Standing Committee on the Henry M. Phillips' Prize Essay Fund.

*Sixth.* All amounts of interest accruing and unexpended on each and every occasion on which no prize shall be awarded, shall be considered and taken as accretions to the principal of the said fund.

*Seventh.* All essays may be written in English, French, German, Dutch, Italian, Spanish or Latin ; but, if any language except English, must be accompanied by an English translation of the same.

*Eighth.* No treatise or essay shall be entitled to compete for the prize that has been already published or printed, or for which the author has received already any prize, or profit, or honor, of any nature whatsoever.

*Ninth.* All essays must be clearly and legibly written on only one side of the paper.

*Tenth.* The literary property of such essays shall be in their authors, subject to the right of the Society to publish the crowned essays in its Transactions or Proceedings.

*Eleventh.* A Standing Committee, to consist of five members appointed by the President, and *ex officio*, the President and the Treasurer of the Society, shall continue in office during the pleasure of the Society, and any vacancies that may occur in said Committee shall be filled by new appointment by the President.

*Twelfth.* The said Committee shall have charge of all matters connected with the management of this endowment and the investment of the same, and shall make such general rules for publishing the terms upon which said prize shall be competed for, and the amount of the said prize, and, if it shall deem it expedient, designate the subjects for competing essays. It shall report annually to the Society, on the first Friday in December, all its transactions, with an account of the investment of the Prize Fund, and of the income and expenditures thereof.

*The first prize to be awarded by the Society will be the sum of one thousand dollars, lawful gold coin of the United States of America, and all treatises in competition therefor must be in the possession of the Society before the first day of January, 1893.*

*The prize will be awarded for "The best Treatise on the History and Growth of the Philosophy of Jurisprudence, divided into Ancient, Mediæval and Modern Periods, presenting a complete conspectus of the literature, bibliography and opinion pertaining to the subject."*

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*Eleventh.* The said Committee shall have charge of all matters connected with the management of this endowment and the investment of the same, and shall make such general rules for publishing the terms upon which said prize shall be competed for, and the amount of the said prize, and if it shall deem it expedient, designate the subjects for competing essays. It shall report annually to the Society, on the first Friday in December, all its transactions, with an account of the investment of the Prize Fund, and of the income and expenditures thereof.

*An award of the Prize will be made during the year 1895; essays for the same to be in the possession of the Society before the first day of January, 1895. The subjects upon which essays are to be furnished by competitors are as follows:*

> *1. The sources, formation and development of what is generally designated the Common Law of England.*
>
> *2. The theory of the State, treated historically and upon principle, with a discussion of the various schools of classical, mediæval, and modern thought upon the subject.*
>
> *3. The historical and doctrinal relations of the Roman Law and the English Law, illustrated by parallels and contrasts.*

*The Prize for the crowned essay on either of these subjects will consist of the sum of five hundred dollars lawful gold coin of the United States, to be paid upon the awarding of the Prize.*

*The essays must be sent, addressed to Frederick Fraley, President of the American Philosophical Society, Hall of the Society, No. 104 South Fifth Street, Philadelphia, Pa.*

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