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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

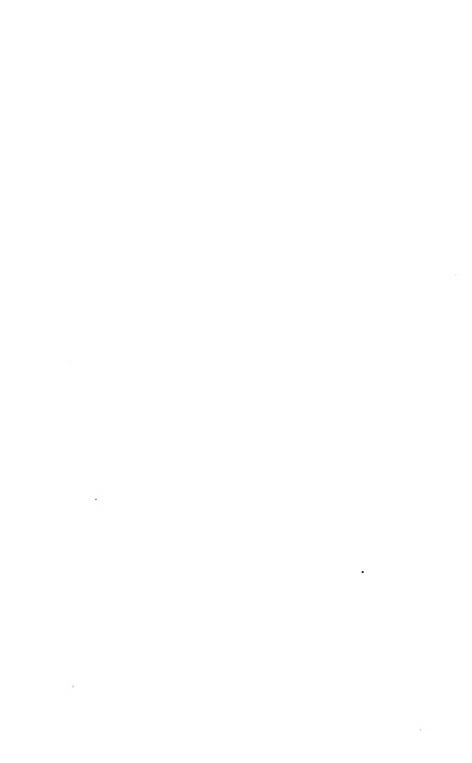
#### STUDIES ON FLUORITE.

IV. — THE KATHODO-LUMINESCENCE OF FLUORITE.

BY HARRY W. MORSE.

WITH A PLATE,

Investigations on Light and Heat made and published, wholly or in part, with Appropriation from the Rumford Fund.



# CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

#### STUDIES ON FLUORITE.

#### IV. THE KATHODO-LUMINESCENCE OF FLUORITE.

By HARRY W. MORSE.

Presented by John Trowbridge. Received March 20, 1907.

I. In previous papers which have been presented to the American Academy by the author, data on the light emitted by crystals of fluorite from various localities, excited by light <sup>1</sup> and by heat, <sup>2</sup> have been discussed. The present research contains data on the spectra of the light emitted by various fluorites under excitation by kathode rays.

It was found in the first research that many fluorites, if not all, give discontinuous spectra when excited by the light from certain sparks. The metals which have strong ultra-violet lines in their spark spectra, used as terminals for the passage of a strong spark, excite lines of fluorescence in these fluorites; and while these lines are in most cases somewhat diffuse and broad in appearance, they are in other cases apparently as sharp as the metallic lines which excite them.

In the later paper, data has been given on the light emitted, in two typical cases, by fluorites under excitation by heat alone. Here again the spectra are discontinuous, and contain, beside broad-banded portions, lines which are quite sharp.

The spectroscopic side of the luminescence of fluorite is not exhausted by a study of the fluorescence and thermo-luminescence spectra. This mineral is most remarkable in the great variety of ways by which its luminescence can be excited, and it is known to emit light under the influence of kathode rays, X-rays, and radium radiation, as well as by simply rubbing or breaking a crystal.

Parallel with the spectroscopic investigation of the light emitted by the crystals under various excitations, a careful series of investigations

<sup>2</sup> Studies on Fluorite, II. These Proceedings, 41, 593 (Mar. 1906).

<sup>&</sup>lt;sup>1</sup> The Fluorescence Spectrum of Fluorite, Astrophysical Journal, **21**, 83 (Mar. 1905); Studies on Fluorite, I. These Proceedings, **41**, 587 (Mar. 1906).

has been made on the impurities which are present in the natural mineral. The first of these investigations <sup>3</sup> was made on the gases contained in fluorite, and the results of this research are wholly negative as far as the question of the source of luminescence is concerned. Nothing other than the ordinary gases was found in any case, and no relation between the occluded gases and the emission of light under excitation was discovered.

At the present time, careful chemical analyses of a series of fluorites from many parts of the world are being carried out, in the hope of finding a clue to the source of the light-emission. The results of these analyses, as far as they have gone, are most interesting. Many fluorites are found to contain quite evident amounts of rare earths, and from one specimen, at least, enough neodymium and praseodymium have been separated to give a quite measurable absorption spectrum. The author intends to report the results of these investigations to the American Academy as soon as possible.

- II. The spectra of a large number of fluorites, excited by kathode rays, have been examined and photographed. Of this large number, seven will be described in this paper. The crystals examined were:
- 1. Fluorite from Amelia Court-House, Virginia. This region is a famous one because of the occurrence of this fluorite, which has remarkable properties, and also for many other minerals containing rare earths. Very large microlite crystals were found near the fluorite deposits. The crystals of fluorite from this region are what are called "chlorophanes," par excellence. They are very sensitive to heat, emitting light strongly at the temperature of boiling water, and so strongly at 300° as to be bright objects even in a well-lighted room. The fluorites occur in colors varying from dark brown and dark purple to light green. All show the same thermo-luminescence spectrum, and the same kathodo-luminescence spectrum. The spectrum of thermo-luminescence of this variety has been given at length in a previous paper. The details of the kathodo-luminescence spectrum are given in Table I, and the appearance of this spectrum is seen in Figure 1, Plate o.
- 2. Fluorite from Trumbull, Conn. This is also a brilliant "chlorophane," which shows the same thermo-luminescence spectrum as the Virginia crystals, and a kathodo-luminescence spectrum which is very closely related to that of the other mineral. Details of the latter spectrum are given in Table II, and the appearance of the spectrum is seen in Figure 2 of the plate.

<sup>3</sup> Studies on Fluorite, III. These Proceedings, 41, 601 (Mar. 1906).

<sup>&</sup>lt;sup>4</sup> See also Humphreys, Astrophysical Journal, 20, 266 (1904).

<sup>&</sup>lt;sup>5</sup> Studies on Fluorite, H. These Proceedings, 41, 593 (Mar. 1906).

3. Fluorite from Westmoreland, N. H. This is a clear, light-green fluorite, which shows no very strong fluorescence, but which is most brilliant in thermo-luminescence, giving out a purple light, the spectrum of which has been fully described in a previous paper.<sup>6</sup> Its kathodo-luminescence spectrum is in many respects very different from all the others described. The details of this spectrum are given in Table III, and a photograph of the spectrum is reproduced in Figure 3 of the plate.

4. Fluorite from Hardin County, Ohio. This is a clear pink variety of no very strong fluorescence or thermo-luminescence, but which shows a fairly strong kathodo-luminescence. Its spectrum is shown in

Figure 4, and the detail of the lines is given in Table IV.

5. Purple fluorite from Weardale, England. This locality has furnished some of the most beautiful fluorspar crystals of the world, and this particular crystal was cut from a large and perfect natural crystal. It is the same crystal as No. 5 of the paper on the fluorescence of fluorite, 7 and it is characterized by a fine series of layers of different colors, in planes parallel to the natural faces of the crystal. (Table V and Figure 5.)

6. Green Weardale crystal. A deep green variety from the same locality, showing a kathodo-luminescence spectrum very much like that of the purple variety, but different in some strong lines. Table VI, of wave-lengths, and Figure 6 of the plate, show its characteristics.

7. Yellow Weardale crystal. From the same locality, but of deep straw-yellow color. Not very strong in fluorescence or thermo-luminescence, but giving a fine purple kathodo-luminescence. Shown in Figure 7 and described in Table VII.

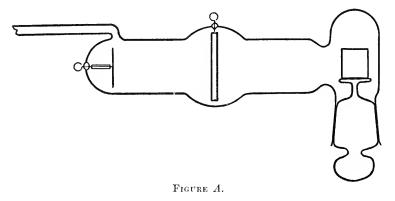
III. After the preliminary study of the method, exposure, conditions for brightest luminescence, etc., the crystals described were cut from the natural crystals and their faces polished. This treatment permits of excluding the lines of gases in the tube as completely as possible, and gives a field of light which is regular and smooth. The crystals were then mounted in the vacuum tube so that one of the polished faces was exposed directly to the kathode bombardment, the spectroscope being so placed that it would take in all the light possible from the polished face of the crystal.

The form of tube shown in the figure (Figure A) is convenient for this special purpose. The crystal is mounted on the little table which forms the end of the stop-cock, and so mounted it can be turned

<sup>&</sup>lt;sup>6</sup> Studies on Fluorite, II. These Proceedings, 41, 593 (Mar. 1906).

<sup>&</sup>lt;sup>7</sup> The Fluorescence Spectrum of Fluorite, Astrophysical Journal, **21**, 83 (Mar. 1905); Studies on Fluorite, I. These Proceedings, **41**, 587 (Mar. 1906).

to any desired position in front of the rays, or a new face can be exposed when this is necessary, without loss of time. In the preliminary examination, a number of small bits of fluorite were mounted on the revolving table, near the edge, and these could then be brought one after the other into the kathode rays, and their spectra studied with a hand spectroscope. During the entire research the kathode stream was controlled by means of a permanent magnet, and with it the brightest luminescence could be brought out near the slit; or, if the crystal had been mounted a little too low or too high, the kathode stream was brought into the most favorable position for bright luminescence by means of the magnet.



The large aperture spectroscope already described <sup>8</sup> was used for the photography of the spectra, and Cramer Tri-chromatic plates were found to give a fairly flat spectrum down as far as wave-length 6000.

It was found that the time of exposure could not be increased beyond a certain point with any advantage. The well-known phenomenon of discoloration of the crystal faces takes place, and before long the layer of color becomes so dense that practically no more kathode excitation gets through it, and the luminescence stops. About half an hour is the limit of profitable exposure for a single crystal face under the conditions of excitation used in this work, and if the intensity of the kathode stream is greatly increased, this time is reduced to a few minntes. The time varies with different crystals, and some of them remain unattacked for a much longer period than others. When a longer exposure than half an hour was found necessary, the crystal was simply

<sup>8</sup> The Fluorescence Spectrum of Fluorite, Astrophysical Journal, 21, 83 (Mar. 1905); Studies on Fluorite, I. These Proceedings, 41, 587 (Mar. 1906).

turned through 90° and a new face presented, so that the exposure could be continued to about two hours with a single crystal. The luminescence light passes almost undimmed through the thin layer of color on the face of the crystal, so that a face which has been completely protected from further excitation by the kathode beam is still quite transparent to light, and may therefore be turned toward the slit, while a new face is exposed to excitation.

The tube was kept connected with the pump during the entire series of experiments, and the vacuum was brought back to the most favorable point whenever necessary. For some crystals no pumping was required, and the vacuum remained at the right point for many hours. In other cases constant use of the pump was necessary. The Westmoreland crystal (No. 3), although one of the clearest and least colored of the series, gave off hydrogen in measurable quantities, and the spectrum of the gases in the tube changed slowly after this crystal was introduced. until finally the original nitrogen (air) spectrum had almost entirely disappeared and only hydrogen was visible. This is evidently closely connected with the fact that this same Westmoreland fluorite contains a considerable percentage of hydrogen in the gases which it holds occluded. Analysis of the gases given off from this fluorite on heating showed that while the amount of gas present was small compared with some other fluorites, it contained about 52 per cent of hydrogen.9 The evolution of hydrogen at room temperature, under the influence of the kathode discharge, is an interesting qualitative confirmation of the analyses.

IV. In the following tables the abbreviations

sh., sharp dif., diffuse q. sh., quite sharp v. sh., very sharp v. dif., very diffuse max., maximum

are used. Bands are indicated by brackets enclosing the numbers representing their boundaries.

Intensities are given on a scale of 1 to 10, increasing.

In tables IX and X the strong lines and those common to several crystals have been collected. A few important relations may be mentioned.

The band from  $\lambda$  5570 to  $\lambda$  5610 is a universal constituent of all these spectra.

The strong line at  $\lambda$  5667 is present in all but one. It is just as cer-

<sup>&</sup>lt;sup>9</sup> See also Humphreys, Astrophysical Journal, **20**, 266 (1904).

tainly absent from the spectrum of the Ohio crystal, and it is replaced by the line at  $\lambda$  5676.

Table X shows the most common lines and their occurrence in the seven spectra under analysis. Comparison with the tables of wave-

TABLE I.

Amelia Court House (Va.) Fluorite.

| Wave-lengtl | . Intensity. | Remarks.   | Wave-length | h. Intensity. | Remarks.     |
|-------------|--------------|------------|-------------|---------------|--------------|
| 4310        | $^2$         |            | (5375       |               |              |
| 4332        | 1            |            | { to        | strong        | band.        |
| 4350        | 3            | q. sh.     | 5407        | 9             |              |
| (4360)      |              | •          | 5455        | $^2$          | dif.         |
| d to ra     | ther weak ba | ınd.       | 5535        | $^2$          | dif.         |
| (4378       |              |            | 5608        | $^2$          | dif.         |
| 4415        | $^2$         | dif.       | (5665       | 10            |              |
| 4544        | $^2$         |            | to          |               |              |
| 4663        | 2            |            | 5733        | max.          | strong band. |
| 4775        | $^2$         |            | to          |               |              |
| { (4800     |              |            | \5780 sl    | narp edge.    |              |
| 1 to        | rather       | weak band. | [5804       |               |              |
| \\4832      |              |            | to          |               | weak band.   |
| 4857        | 3            | q. sh.     | 5886        | 3             |              |
| 5295        | 1            | dif.       | 5962        | $^2$          | dif.         |
| 5332        | 1            | dif.       | 6040        | 3             | dif.         |

TABLE II.

TRUMBULL, CONN., FLUORITE.

| Wave-leng           | th. Intensity.  | Remarks.     | Wave-length. | Intensity. | Remarks.       |
|---------------------|-----------------|--------------|--------------|------------|----------------|
| 4145                | 1               | dif.         | 5666         | 8 ra       | ther dif.      |
| 4335                | 3               | dif.         | 5693         | $^2$       |                |
| 4350                | 5               | q. sh.       | 5710         | 2          | dif.           |
| (4365               |                 |              | 5731         | 3          | v. sh.         |
| } to s              | strong flat ban | $\mathbf{d}$ | 5750         | 5          | v. sh.         |
| $(_{4380}$          | _               |              | 5774         | 8          | v. sh.         |
| 4417                | 5               | dif.         | (5795        |            |                |
| 4510                | 1               | dif.         | to           |            | $_{ m band}$ . |
| 5398                | 5               | broad.       | 5837         |            |                |
| 5433                | 1               |              | (5860        |            |                |
| 5487                | 2               |              | to           |            | band.          |
| 5506                | 2               |              | 5890         |            |                |
| 5539                | 4               | broad.       | 6055         | 2          | dif.           |
| (5555)              |                 |              |              |            |                |
| to                  | rather          | weak band.   |              |            |                |
| <sup>1</sup> 5610 s | sharp edge      |              |              |            |                |

lengths of the spectra produced by fluorescence <sup>10</sup> and by thermo-luminescence <sup>11</sup> shows immediately that while the spectra are similar in general appearance, and while the strong lines in the kathodo-spectra are in about the same part of the spectrum as those in the fluorescence-spectra, there are no coincidences of importance. The three luminescences are totally different as far as the wave-lengths of the principal lines are concerned. And a moment's consideration of the facts about

TABLE III.
WESTMORELAND, N. H., FLUORITE.

| Wave-length. | Intensity. | Remarks. | Wave-length. Intensity. Remarks.      |
|--------------|------------|----------|---------------------------------------|
| 4722         | 2          | v. dif.  | (5573 3                               |
| 4777         | $^2$       | v. dif.  | to band.                              |
| 4857         | 4          | q. sh.   | ( 5608                                |
| 4892         | $^2$       | dif.     | 5667 4 dif.                           |
| 5142         | 1          | dif.     | 5727 4 q. sh.                         |
| 5187         | $^2$       | dif.     | (5767 max. or sh. edge                |
| 5244         | <b>2</b>   | dif.     | \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ |
| 5332         | 1          |          | 5822                                  |
| 5370         | 5          | q. sh.   | ( 5870                                |
| 5398         | 5          | q. sh.   | to diffuse band.                      |
| 5433         | 1          | •        | ( 5912                                |
| 5468         | $^2$       | q. sh.   | ( 5980                                |
| 5513         | 8          | dif.     | to weak band with 2 max.              |
|              |            |          | 6055                                  |

TABLE IV.

FLUORITE FROM HARDIN CO., ILL.

| Wave-length | . Intensity.   | Remarks. | Wave-lengtl | h. Intensity. | Remarks.  |
|-------------|----------------|----------|-------------|---------------|-----------|
| 4898        | <b>2</b>       | dif.     | 5676        | 10            | q. sh.    |
| 5192        | $^2$           | dif.     | 5735        | 3             | q. sh.    |
| 5262        | 1              | dif.     | (5767       |               | •         |
| 5345        | 1              |          | to          |               |           |
| 5375        | 5              | q. sh.   | \ \ 5783 r  | max.          | band.     |
| 5400        | 5              | q. sh.   | to          |               |           |
| 5434        | 1              |          | 5822        |               |           |
| 5468        | 3              | q. sh.   | (5872       |               |           |
| 5517        | 2              | dif.     | { to        | fairly stro   | ong band. |
| 5538        | 1              | q. sh.   | ( 5914      |               |           |
| ( 5572      |                |          | (5978       |               |           |
| of to fa    | irly strong ba | ınd.     | { to        |               | band.     |
| 5619        |                |          | 6053        | max.          |           |

The Fluorescence Spectrum of Fluorite, Astrophysical Journal, 21, 83, (Mar. 1905); Studies on Fluorite, I. These Proceedings, 41, 587 (Mar. 1906).
 Studies on Fluorite, II. These Proceedings, 41, 593 (Mar. 1906).

the fluorescence spectra makes this result necessary as far as that method of excitation is concerned. The fluorescence spectrum of a crystal of fluorite is a function of the exciting source, and changes completely when the exciting wave-lengths are changed. It is therefore improbable that any one of the fluorescence spectra should show more than approximate or accidental coincidences with many lines excited by either heat or kathode luminescence. There are lines which appear in the fluorescence spectra of a crystal under excitation by several different sources,

TABLE V.

Purple Weardale (Eng.) Fluorite.

| Wave-length. | Intensity. | Remarks. | Wave-length. | Intensity. Remarks. |
|--------------|------------|----------|--------------|---------------------|
| 4727         | 1          |          | 5669         | 10 rather dif.      |
| 4782         | 1          |          | 5754         | max. in band.       |
| 4796         | 1          |          | 5780         | 4 max. of band.     |
| 4944         | $^2$       |          | (5810 max.   |                     |
| 5337         | 1          |          | { to         | band.               |
| 5374         | 3          |          | ( 5857       |                     |
| 5407         | 5          |          | ( 5871       |                     |
| 5467         | 3          |          | } to         | rather weak band.   |
| 5509         | $^2$       |          | ( 5908       |                     |
| 5542         | 3          |          | 6045         | 5                   |
| (5571        |            |          | 6114         | 1                   |
| { to         |            | band.    |              |                     |
| ( 5612       |            |          |              |                     |

TABLE VI.

GREEN WEARDALE (ENG.) FLUORITE.

| Wave-length. | Intensity. | Remarks.   | Wave-length. | Intensity.         | Remarks.    |
|--------------|------------|------------|--------------|--------------------|-------------|
| 4730         | 4          | q. sh.     | 5517         | 1                  | dif.        |
| 4780         | 3          | $\sinh$ .  | 5537         | 3                  | q. sh.      |
| 4795         | 4          | sh.        | ( 5575       | $^2$               | 1           |
| (4854        |            |            | { to         |                    |             |
| } to         | rather     | weak band. | ( 5606       | $^2$               | band.       |
| (4867        |            |            | 5667         | $10  \mathrm{sh}.$ | and strong. |
| 4890         | 1          | dif.       | 5726         | 3                  | q. sh.      |
| 4915         | 3          | broad.     | 5761         | 1                  |             |
| 4947         | 1          | dif.       | 5774         | 5                  | q. sh.      |
| 5333         | 1          | broad.     | 5809         | 5                  | q. sh.      |
| 5370         | 3          | q. sh.     | 5833         | 5                  | q. sh.      |
| 5396         | 1          | q. sh.     | ( 5861       | sharp              | edge here.  |
| 5408         | 5          | q. sh.     | { to         | strong             | band.       |
| 5439         | 2          | broad.     | ( 5893       |                    |             |
| 5470         | 5          | broad.     | 6040         | 8                  | q. sh.      |
| 5506         | 2          | q. sh.     | 6110         | 1                  | q. sh.      |

and these might be expected to be a property of the crystal, and to persist under other forms of excitation. None of these lines appear in either the thermo-luminescence or kathodo-luminescence of these crystals. That the same substance can, however, give the same spectrum under excitation by light and by heat has been shown by Becquerel, <sup>12</sup> and Urbain <sup>13</sup> has proven that the same spectrum, modified only slightly, is shown by the same substance under excitation by kathode rays. The necessary conclusion from the author's experiments is, however, that this is by no means always the case. The purple Weardale fluorite (No. 5) has been most carefully studied both in fluorescence and in kathodo-luminescence, and there is no relation whatever between these spectra as far as the wave-lengths of lines are concerned. The Westmoreland fluorite, and that from Amelia Court-House, have been investigated in both thermo-luminescence and kathodo-luminescence, and no coincidences of importance are visible.

Plate **o** gives a very good idea of the relation between the kathodoluminescence spectra of the seven crystals examined. The two upper spectra are very evidently similar. They are both "chlorophanes,"

TABLE VII.
YELLOW WEARDALE (ENG.) FLUORITE.

| Wave-length.      | Intensity.  | Remarks. | Wave-length.                 | Intensity. | Remarks.   |
|-------------------|-------------|----------|------------------------------|------------|------------|
| 4332              | $^2$        |          | 4946                         | 1          | dif.       |
| 4350              | 8           | sh.      | 5372                         | $^2$       |            |
| (4365             |             |          | 5400                         | 1          |            |
| $\exists$ to broa | d flat band |          | 5408                         | 2          |            |
| (4382             |             |          | 5437                         | 1          |            |
| 4419              | 8           | dif.     | 5470                         | 3          | q. slı.    |
| 4512              | $^2$        |          | (5508                        | $^2$       | q. sh.     |
| ( 4542            | 4           | dif.     | \ \ \ to                     | ban        | d between. |
| to                |             |          | 5540                         | $^2$       | q. sh.     |
| (4705             | $^2$        | dif.     | (5570                        |            |            |
| 4736              | 8           | q. sh.   | to                           |            |            |
| 4752              | $^2$        |          | $\frac{1}{\sqrt{5602}}$ max. | a br       | oad band.  |
| 4767              | 1           |          | to                           |            |            |
| 4785              | 5           | sh.      | \5615                        |            |            |
| 4796              | 5           | sh.      | 5669                         | 10         | q. sh.     |
| (4814             | 2           |          | 5730                         | 2          | q. sh.     |
| { to              |             | band.    | 5773                         | 3          | q. sh.     |
| 4833              | 1           |          | 5811                         | 2          | q. sh.     |
| 4860              | 4           | dif.     | 5837                         | 1          | q. sh.     |
| 4917              | 4           | dif.     | 5885                         | 3          | dif.       |

<sup>&</sup>lt;sup>12</sup> Journal de physique, **68**, 414, and **69**, 169.

<sup>&</sup>lt;sup>13</sup> Comptes rendus, **143**, 825 (1906).

#### TABLE VIII.

#### SUMMARY.

|              | 1.                    | 2.     | 3.    | 4.    | 5      | 6.     | 7.                 |
|--------------|-----------------------|--------|-------|-------|--------|--------|--------------------|
| Wave-length. | Am. C-H.              | Trumb. | West. | Ohio, | P. Wr. | G. Wr. | Y. Wr.             |
| 4145         |                       | 1 d.   |       |       |        |        |                    |
| 4310         | 2                     | 1 (1.  |       |       |        |        |                    |
| 4333         | ī                     | 3 d.   |       |       |        |        | 2                  |
| 4350         | 3 s.                  | 5 s.   |       |       |        |        | 2<br>8 s.          |
| (4360        |                       | 0 0.   |       |       |        |        |                    |
| ₹ to         | w.                    | st.    |       |       |        |        | st.                |
| 4380         |                       |        |       |       |        |        |                    |
| 4416         | 2 d.                  | 5 d.   |       |       |        |        | 8 d.               |
| 4511         |                       | 1 d.   |       |       |        |        | 2                  |
| 4543         | $\frac{2}{2}$         |        |       |       |        |        | ( 4 d.             |
| 4663         | 2                     |        |       |       |        |        | $\frac{1}{2}$ bnd. |
| 4705         |                       |        |       |       |        |        | ( 2 d.             |
| 4722         |                       |        | 2 d.  |       |        |        |                    |
| 4728         |                       |        |       |       | 1      | 4 s.   |                    |
| 4736         |                       |        |       |       |        |        | 8 s.               |
| 4752         |                       |        |       |       |        |        | 2                  |
| 4767         |                       |        |       |       |        |        | 1                  |
| 4776         | $^2$                  |        | 2 d.  |       |        |        |                    |
| 4781         |                       |        |       |       | 1      | 3 s.   |                    |
| 4785         |                       |        |       |       |        |        | 5 s.               |
| .4796        |                       |        |       |       | 1      | 4 s.   | , 5 s.             |
| 4800         | (                     |        |       | ĺ     |        |        | (2                 |
| 4814         | $\frac{1}{2}$ w. bnd. |        |       |       |        |        | $\beta$ bnd.       |
| 4832         | (                     |        |       | ĺ     |        |        | (1                 |
| 4856         | 3 s.                  |        | 4 s.  |       |        | (      |                    |
| 4860         |                       |        |       |       | ļ      | bnd.   | 4 d.               |
| 4867         |                       |        |       |       |        | (      | i                  |
| 4891         |                       |        | 2 d.  |       | 1      | 1 d.   |                    |
| 4898         |                       |        |       | 2 d.  | ĺ      |        |                    |
| 4917         |                       |        |       |       |        | 3 b.   | 4 d.               |
| 4946         |                       |        | _     |       | 2      | 1 d.   | 1 d.               |
| 5142         |                       |        | 1 d.  | _ ,   |        |        |                    |
| 5190         |                       |        | 2 d.  | 2 d.  |        | 1      |                    |
| 5244         |                       |        | 2 d.  |       |        |        |                    |
| 5262         |                       |        |       | 1 d.  |        |        |                    |
| 5295         | 1                     |        | _     |       | _      |        |                    |
| 5334         | 1                     |        | 1     |       | 1      | 1 b.   |                    |
| 5345         | ,                     |        | _     | 1     |        | .      |                    |
| 5373         | ∫ st.                 | -,     | 5 s.  | 5 s.  | 3      | 3 s.   | 2                  |
| 5397         | bnd.                  | 5 b.   | 5 s.  | 5 s.  | _      | 1 s.   | 1                  |
| 5408         |                       |        |       |       | 5      | 5 s.   | 2                  |
|              |                       |        |       |       |        |        |                    |

TABLE VIII. (Continued.)

|                                               |             | _             |                      |          |                                                 |              | _      |
|-----------------------------------------------|-------------|---------------|----------------------|----------|-------------------------------------------------|--------------|--------|
|                                               | 1.          | 2.            | 3.                   | 4.       | 5.                                              | 6            | 7.     |
| Wave-length.                                  | Am. C-H.    | Trumb.        | West.                | Ohio.    | P. Wr.                                          | G. Wr.       | Y. Wr. |
| 5435                                          |             | 1             | 1                    | 1        |                                                 | 2 b.         | 1      |
| 5455 $5469$                                   | 2 d.        |               | 2 s.                 | 3 s.     | 3                                               | 5 b.         | 3 s.   |
| 5487                                          |             | 2             |                      |          |                                                 |              |        |
| 5508                                          |             | $\frac{2}{2}$ |                      |          | 2                                               | 2 s.         | (2     |
| 5513                                          |             |               | 8 d.                 |          |                                                 |              | 1)     |
| 5517                                          |             |               |                      | 2 d.     |                                                 | 1 d.         | bnd.   |
| 5538                                          | 2 dif.      | 4 b.          |                      | 1 s.     | 3                                               | 3 s.         | \2     |
| 5550                                          |             | (             |                      |          |                                                 | ,            |        |
| 5572                                          |             | $\}$ w. bnd.  | )                    | (        | \                                               | ${}^{2}$     | J      |
| 5610                                          | 2 d.        | (             | (3 bnd.              | st. bnd. | lbnd.                                           | {2 bnd.      | (bnd.  |
| 5666                                          | (10         | 8             | 4 d.                 | 10       | 10                                              | 10 s.        | 10 s.  |
| 5676                                          |             |               |                      | 10 s.    |                                                 |              |        |
| 5693                                          |             | 2<br>2 d.     |                      |          |                                                 |              |        |
| $5710 \\ 5727$                                | bnd.        | 2 a.          | 4 s.                 |          |                                                 | 3 s.         | ٥. ا   |
| $\begin{array}{c c} 5727 \\ 5732 \end{array}$ | m.          | 3 s.          | 4 S.                 | 3 s.     |                                                 | 5 S.         | 2 s.   |
| 5755                                          | 111.        | o s.          | (                    | 0 5.     | d. m.                                           | 1            |        |
| 5772                                          | i           | S s.          | l m.                 |          | (I. III.                                        | 5 s.         | 3 s.   |
| 5782                                          | s.          | 0 5.          | ''''                 | m.       | 4 d.                                            | 0 5.         | 0 5.   |
| 5795                                          |             | (             | bnd.                 | bnd.     |                                                 |              |        |
| 5804                                          | ĺ           | 1             |                      |          |                                                 |              |        |
| 5810                                          |             | bnd.          |                      |          | ιm.                                             | 5 s.         | 2 s.   |
| 5822                                          |             |               |                      | (        | 1                                               |              |        |
| 5833                                          |             |               |                      |          | dond. do de | 5 s.         |        |
| 5837                                          |             |               |                      |          |                                                 |              | 1 s.   |
| 5860                                          |             | (             |                      | Ì        | ,                                               |              |        |
| 5870                                          |             | bnd.          |                      |          |                                                 | (            |        |
| 5885                                          | 3           |               | J                    | 1, ,     | J 1                                             | bnd.         | 3 d.   |
| 5892                                          |             |               | bnd.                 | f bnd.   | bnd.                                            | (            |        |
| 5910                                          |             |               | l j                  | (        |                                                 |              |        |
| 5962                                          | 2 d.        |               |                      |          |                                                 |              |        |
| 5980                                          | 3 d.        |               | $\int_{\text{bnd.}}$ | bnd.     |                                                 | 0 ~          |        |
| 6040                                          | <b>ઝ</b> લ. |               | Jona.                | y ona.   | 5                                               | 8 s.         | - 1    |
| 6045<br>6054                                  |             | 2 d.          | $\binom{1}{m}$       |          | Э                                               | 1 s.         | l      |
| 6112                                          |             | u. ا          | `111.                |          | 1                                               | 1 s.<br>1 s. | - 1    |
| 0112                                          |             |               | !                    |          | 1                                               | 1 8.         | - 1    |

(In the above summary s., sharp; d., diffuse; m., maximum in band; w., weak; bnd., band; st., strong; are used. Bands are indicated by brackets.)

TABLE IX.

STRONG LINES.

AND THOSE COMMON TO SEVERAL CRYSTALS.

| Wave-length.         | Am. C-H.     | Trumb.       | West.                                 | Ohio. | P. Wr.           | G. Wr. | Y. Wr.                |
|----------------------|--------------|--------------|---------------------------------------|-------|------------------|--------|-----------------------|
| 4350<br>4416         | 3 s.<br>3 d. | 5 s.<br>5 d. |                                       |       |                  |        | 8 s.<br>8 d.          |
| 4730                 | ou.          | ou.          | 9                                     |       | 1                |        | 4 4                   |
| 4780                 |              |              | $\begin{array}{c} 2 \\ 2 \end{array}$ |       | 1                | 3      | 1 4                   |
| 4785                 |              |              | _                                     |       |                  | "      | 5                     |
| 4796                 |              |              |                                       |       |                  | 4      | 5<br>5                |
| 4856                 | 3 s.         |              | 4 s.                                  |       |                  | 1      | 4 d.                  |
| 4917                 |              |              | 10,                                   |       |                  | 3      |                       |
| 5372                 |              |              | 5                                     | 5     | 3                | 3 3    | 4<br>3<br>1<br>5<br>3 |
| 5398                 |              | 5            | 5                                     | 5     |                  | 1      | 1                     |
| 5408                 |              |              |                                       |       | 5                | 1<br>5 | 5                     |
| 5470                 | i            |              | 2<br>8                                | 3     | 5<br>3<br>2<br>3 | 5      | 3                     |
| 5512                 |              |              | 8                                     |       | 2                |        |                       |
| 5538                 | 2            | 4            | İ                                     | 1     | 3                | 3      | 2                     |
| ( 5570               | 1            |              |                                       |       |                  |        |                       |
| $\left\{ \right.$ to | bnd.         | bnd.         | bnd.                                  | bnd.  | bnd.             | bnd.   | bnd.                  |
| ( 5610               |              |              |                                       |       |                  |        |                       |
| 5667                 | 10           | 8            | 4                                     |       | 10               | 10     | 10                    |
| 5676                 |              |              |                                       | 10    |                  |        |                       |
| 5730                 |              | 3            | 4                                     | 3     | l                | 3      | 2                     |
| 5775                 | m.           | 8            | m.                                    | m.    | 4                | 5      | 3 2 3                 |
| 5810                 | bnd.         | bnd.         | bnd.                                  | bnd.  | m.               | 5      | 2                     |
| 5885                 | 3            | bnd.         | bnd.                                  | bnd.  | bnd.             | bnd.   | 3                     |
| 6040                 | 3            | bnd.         | bnd.                                  | bnd.  | 5                | 8      |                       |

(s., sharp; d., diffuse; m., maximum in band; bnd., band; intensities on increasing scale of 1 to 10.)

 $\label{table X.} {\rm THE\ Most\ Common\ Lines\ of\ the\ 7\ Crystals.}$ 

| 5372 in<br>5398<br>5538<br>5667<br>5730<br>5775 | 5 5810<br>5 5885<br>6 6050<br>6 or 7 5570<br>5 to 5610 | in 7<br>7<br>6<br>7 |
|-------------------------------------------------|--------------------------------------------------------|---------------------|
|-------------------------------------------------|--------------------------------------------------------|---------------------|

and the spectrum is therefore concealed in some degree beneath the broad green band which is characteristic of both. The similarity in many of the sharper lines is, however, perfectly apparent.

The spectra of Figures 3 and 4 are quite different from each other and from the other spectra shown. The larger part of the luminescence lines are in the same part of the spectrum as in the others, but the lines are not the same. Figure 4 is more like the spectra 5, 6, and 7 than it is like the ones preceding it in the plate. The three lower figures are all of fluorites from Weardale. They are very similar in most of their lines, but show evident differences in the strength of individual lines and groups of lines.

In none of these spectra are the lines quite as sharp as the lines of fluorescence. They are all diffuse in comparison with sharp metallic lines.

While work on this research was in progress, a paper by Urbain 14 appeared in which the cause of the luminescence of fluorite was definitely connected with the presence of the rare earths terbium, samarium, and dysprosium. The particular fluorite which was cited by Urbain was one which had been examined several years before by Becquerel, 15 both in the phosphoroscope and in thermo-luminescence. It is a "chlorophane" which gives a brilliant green luminescence under all of the various methods of excitation, and from the table of wave-lengths which accompanies the paper it is quite evident that the spectrum of this chlorophane in kathodo-luminescence is very similar in all important details to the spectra of the chlorophanes of the author's Tables I and II, and of Figures 1 and 2. But the resemblance of this spectrum to the kathodo-luminescence spectra of terbium, samarium, and dysprosium, dissolved in various oxides and sulphates, is very slight indeed, and Urbain's conclusions from this resemblance may possibly be unjustified. He prepared from the fluorite in question substances which did give spectra corresponding in every detail with the spectra of the rare earths, and also synthesized a fluorite, which was like the original one, from such preparations. The proof seems a very strong one, but it is one which requires further test. The kathodo-luminescence spectra of the rare earths, in spite of their perfectly definite appearance and their evident persistence as a property of some definite substance or element, have proven most elusive. Crookes <sup>16</sup> spent some fifteen years in fol-

<sup>14</sup> Comptes rendus, 143, 825 (1906).

<sup>15</sup> Journal de physique, **68**, 444, and **69**, 169.

<sup>&</sup>lt;sup>16</sup> A large number of papers by Crookes on this subject are to be found in the Proceedings of the Royal Society, the Transactions, and in the Chemical News, from 1880 to 1890 especially.

lowing certain definite bands in these spectra. Lecoq <sup>17</sup> about as long Baur and his students thought that they had settled the matter finally. <sup>18</sup> Urbain <sup>19</sup> has done wonderful work in separating the elements of the rare earths, and his opinion is undoubtedly of more importance than that of any one else. An explanation along these lines must include not only the case of a single chlorophane, but it must cover also the cases where the fluorescence, thermo-luminescence, and kathodo-luminescence of the same crystal of fluorite are all different, even in their minute details.

While the author cannot expect to test the question by synthesis, further study of the rare elements which are present in fluorites is already under way, and examination of the light emitted by these same fluorites under excitation by other means will also be taken up as soon as possible.

The author's thanks are due to the American Academy for a generous appropriation from the Rumford Fund, which has been of the utmost assistance in this work.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY. March 20, 1907.

<sup>&</sup>lt;sup>17</sup> Papers by Lecoq de Boisbaudran on this subject, to the number of thirty or more, are to be found in the Comptes rendus, beginning with volume **100**, and continuing for many years.

<sup>&</sup>lt;sup>18</sup> Ber. d. d. Chem. Ges., **33**, 1748, and **34**, 2460.

<sup>19</sup> A very complete bibliography of all the literature on the yttrium and cerium earths is that of Meyer, Bibliographie der seltenen Erden. (Leopold Voss, Leipzig, 1905.)

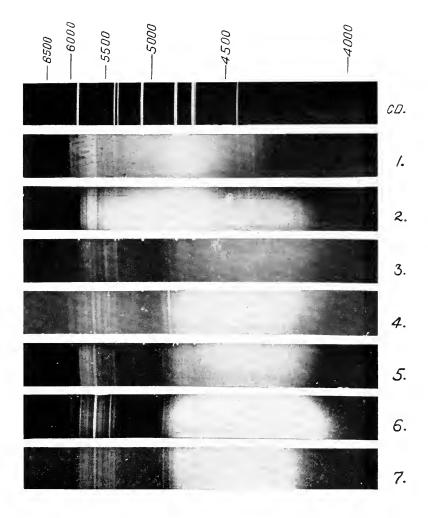


#### EXPLANATION OF PLATE.

The upper spectrum is that of the spark between eadmium terminals, and the numbers indicate wave-lengths.

The seven numbered spectra are kathodo-luminescence spectra of the following:

- 1. Fluorite from Amelia Court-House, Virginia.
- 2. Fluorite from Trumbull, Coun.
- 3. Fluorite from Westmoreland, N. H.
- 4. Fluorite from Hardin Co., Ohio.
- 5. Purple fluorite from Weardale, England.
- 6. Green fluorite from Weardale, England.
- 7. Yellow fluorite from Weardale, England.



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# CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

#### New Series. -- No. XXXIV.

- New Species of Senecio and Schoenocaulon from Mexico. By J. M. Greenman.
- II. New or otherwise Noteworthy Spermatophytes, chiefly from Mexico. By B. L. Robinson.
- III. New Plants from Guatemala and Mexico collected chiefly by C. C. Deam. By B. L. Robinson and H. H. Bartlett.
- IV. Diagnoses of New Spermatophytes from Mexico. By M. L. Fernald.



# CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.—NEW SERIES, NO. XXXIV.

Presented by B. L. Robinson, February 12, 1907. Received February 23, 1907.

# I. NEW SPECIES OF SENECIO AND SCHOENOCAULON FROM MEXICO.

#### By J. M. GREENMAN.

Schoenocaulon calcicola Greenman, n. sp., bulbis ovoideis 1.5-2 cm. diametro; caudice erecto cylindrato 5-10 cm. longo a reliquis atrobrunneis vel nigrescentibus fibrosis squamarum foliorumque exteriorum circumdato; foliis lineari-attenuatis 3-10 dm. longis 2-5 mm. latis 7-13-nerviis utrinque laevibus margine paulo hirtellis; scapo nudo 5.5-7.5 dm. alto aliquanto flexuoso subancipiti glabro basin versus purpureo; inflorescentia laxiflora 1-2 dm. longa 8-10 mm. anthesi diametro; bracteis parvis late ovatis tenuibus brunnescentibus; floribus sessilibus vel breviter pedicellatis; perianthio 6-partito, segmentis linearibus 2.5-3 mm. longis acutiusculis saepissime basi bidentatis; staminibus perianthio longioribus; capsulis maturis oblongo-lanceolatis ca. 1 cm. longis glabris reflexis. — Hillsides, Las Sedas, Oaxaca, Mexico, alt. 1830 m., 1 August, 1894, C. G. Pringle, no. 5754 (type, in hb. Gray); calcareous banks, Las Sedas, alt. 1830 m., 19 July, 1897, C. G. Pringle, no. 6740 (hb. Gray, hb. Field Mus.). The latter number was distributed as S. intermedium Baker, a species from which S. calcicola is readily separated by its reflexed fruit.

Schoenocaulon caricifolium Greenman, n. comb. Veratrum caricifolium Schlecht. Ind. Sem. Hort. Hal. 8 (1838). Asagraea caricifoliu Kunth, Enum. Pl. iv. 666 (1843). Although this species has been treated by several authors as conspecific with Schoenocaulon officinale Gray, yet an examination of some of the original material, collected by Ehrenberg, of which there is now a specimen in the Gray Herbarium, shows very clearly that it can scarcely be regarded as identical with Dr. Gray's species. S. caricifolium differs from S. officinale in having narrower leaves, shorter scapes and inflorescence, and relatively shorter and distinctly inflated capsules. — Mexico, without defi-

nite locality, *Ehrenberg* (hb. Gray). Specimens secured by C. Conzatti and V. González at Etla, Cañada de San Gabriel, State of Oaxaca, alt. 3000 m., 8 August, 1897, no. 323 (hb. Gray), are apparently referable to this species.

Schoenocaulon Ghiesbreghtii Greenman, n. sp., caudice erecto 10-12 cm. alto reliquis brunneis aut nigrescentibus fibrosis squamarum et foliorum primorum obtecto; foliis linearibus attenuatis 4-8 dm. longis 2-6 mm. latis 7-13-nerviis utrinque glabris; inflorescentia 1-1.2 dm. vel ultra longa 1.5-2 cm. diametro densiflora; bracteis late ovatis 2.5 mm. longis obtusis 5-nerviis; floribus sessilibus vel breviter pedicellatis; perianthio profunde 6-partito, lobis anguste oblongis 4-4.5 mm. longis obtusis integris vel subintegris 3-5-nerviis; flamentis perianthio duplo vel ultra longioribus uniforme recurvatis; fructu ignoto. — State of Chiapas, Mexico, without more precise locality, Dr. Ghiesbreght, no. 672 (type, in hb. Gray); without definite locality, alt. 2130 m., Berendt (hb. Gray). This species is rather striking on account of the recurved filaments. In this respect it resembles S. tenuifolium Robinson & Greenman, but in other and more essential characters it is amply distinct.

Schoenocaulon jaliscense Greenman, n. sp., bulbis oblongoovoideis 2.5-3.5 cm. diametro; caudice erecto cylindrato 1-1.5 dm. alto a reliquis atrobrunneis vel nigrescentibus fibrosis squamarum foliorumque exteriorum obtecto; foliis gramineis 6-10 dm. longis 2-7 mm. latis 9-13-nerviis utrinque glabris margine inconspicue hirtellis: scapo erecto 8 dm. vel ultra alto nudo subancipiti aliquid glauco: inflorescentia elongata 1 usque ad fere 5 dm. longitudine 1-1.5 cm, diametro simplici vel raro ramum lateralem gerenti : bracteis parvis scariosis suberoso-marginatis; floribus breviter pedicellatis; perianthio alte 6-partito, segmentis lineari-oblongis ca. 2.5 mm. longis integris vel basi bidentatis apicem obtusum versus paulo ampliatis incrassatisque; staminibus perianthio longioribus; filamentis persistentibus; capsulis immaturis nec non pedicellis et segmentis perianthii plus minusve glaucis et purpurascentibus; fructu erecto oblongo-ovato quam 1 cm. breviore. — Cool grassy sides of cañons, near Guadalaiara. Jalisco, Mexico, 11 November, 1889, C. G. Pringle, no. 2938 (type, in hb. Gray); Rio Blanco, Guadalajara, 1903, C. G. Pringle, no. 11,853 (hb. Gray); Cerro de San Felipe, Oaxaca, Mexico, alt. 2000 m., 29 August, 1897, C. Conzatti & V. González, no. 449 (hb. Gray).

Senecio (§ Eremophili) ctenophyllus Greenman, n. sp., herbaceus annuus vel perennis basi saepe lignosus; caulibus erectis 3-4 dm. altis simplicibus vel ramosis arachnoideo-tomentosis; foliis lanceolatis 2-9 cm. longis 1-2.5 cm. latis plus minusve pectinato-divisis arachnoideo-

tomentulosis; foliis inferioribus petiolatis, summis sessilibus; inflorescentiis terminalibus corymboso-cymosis tomentosis; capitulis numerosis 8–9 mm. altis heterogamis calyculatis; involucri campanulati squamis ca. 13 lineari-lanceolatis 5 mm. longis acutis nigro-penicillatis ceterum glabratis vel sparsissime tomentulosis; floribus femineis liguliferis 5–8, corollis glabris, ligulis flavis; floribus disci ca. 25; achaeniis canohirtellis. — Barranca below Sandia Station, Durango, Mexico, alt. 2135 m., 15 October, 1905, C. G. Pringle, no. 10,105 (type, in hb. Gray). This species has the general aspect of S. eremophilus Richards., S. chihuahuensis Wats. and S. MacDougalii Heller, but differs from all of them in being tomentulose throughout and in having narrower leaves with mostly simple slender and entire lateral teeth or divisions.

Senecio (§ Tomentosi) loratifolius Greenman, n. sp., herbaceus perennis; caulibus erectis 3 dm. altis lanato-tomentosis; foliis alternis elongato-lanceolatis vel subloratis 0.5-1.7 dm. longis 4-12 mm. latis acutis vel obtusis integris membranaceis juventate supra arachnoideotomentosis denique glabratis subtus persistenter albo-tomentosis; foliis inferioribus basi sensim angustatis et subpetiolatis, superioribus sessilibus et amplexicaulibus; inflorescentiis cymosis terminalibus; capitulis paucis 8-9 mm. altis heterogamis calyculatis; involucris campanulatis tomentosis, squamis ca. 13 lineari-lanceolatis 6-7 mm. longis; floribus femineis ligulatis 8-12, corollis glabris flavis; floribus disci ca. 35 quam squamis involucri vix longioribus; achaeniis hispidulis. — Mountains near Saltillo, Coahuila, Mexico, alt. 2133 m., 5 October, 1905, C. G. Pringle, no. 13,676 (type, in hb. Gray). This species is related to S. umbraculiferus Watson, but differs amply in foliar characters, especially in having thinner leaf-texture, glabrate upper leafsurface, and more distinctly amplexicall upper leaves.

## II. NEW OR OTHERWISE NOTEWORTHY SPERMATO-PHYTES, CHIEFLY FROM MEXICO.

By B. L. Robinson.

Tigridia merelosana Robinson, n. sp., bulbo ovoideo acuminato 4-6 cm. longo 2-3.2 cm. diametro atrobrunneo, radicibus fibrosis; caule gracillimo flexuoso 3 dm. alto saepissime 1-2-foliato glabro modice compresso; foliis basilaribus anguste lanceolato-linearibus attenuatis plicato-nervosis ca. 3 dm. longis ca. 8 mm. latis utrinque viridibus glabris laevibus; foliis caulinis linearibus vel anguste spathiformibus;

spathis saepissime 2 longipedunculatis 3-6-floris, foliolis oblongo-lanceolatis acutissimis 2-4 cm. longis margine tenuibus subscariosis; pedicellis gracillimis 2-3 cm. longis glabris; sepalis purpureis 14 mm. longis 6 mm. latis anguste obovatis obtusis basi angustatis in media parte atromaculatis; petalis ovatis 12 mm. longis acutiusculis cordatis brevissime stipitatis supra mediam partem purpurascentibus tenuibus infra mediam partem flavescentibus firmiusculis 6 mm. latis; columna 4 mm. alta; antheris oblongis apiculatis in summa columna sessilibus; ramis styli 6 filiformibus antheras subaequantibus. — Sierra de Tepoxtlan, Morelos, Mexico, alt. 2350 m., 5 September, 1905, C. G. Pringle, no. 13,657 (type, in hb. Gray).

Amaranthus squamulatus Robinson, n. comb. Scleropus squamulatus Anderss. Om Galapagos-öarnes Veg., Stockh. Akad. Handl. 1853, 162 (1854), & Om Galapagos-öarnes Veg. 60 (1859). Scleropus squarrulosus Anderss. ex Gray, Proc. Am. Acad. v. 169 (1861), by clerical error. Amblogyne squarrulosu Gray, l. c. (1861). Amaranthus squarrulosus Uline & Bray, Bot. Gaz. xix. 170 (1894); Rob. & Greenm, Am. Jour. Sci. l. 147 (1895); Rob. Proc. Am. Acad. xxxviii. 136 (1902).

Schoepfia Pringlei Robinson, n. sp., fruticosa vel arborescens 5 m. alta ramosa; ramis teretibus leviter flexuosis a cortice griseo rugoso tectis; ramulis plus minusve angulatis fuscescenti-puberulis; foliis alternis coriaceis ovato-lanceolatis obtusis vel acutiusculis vel etiam falcato-acuminatis integerrimis opacis utrinque viridibus glaberrimis subtus vix pallidioribus obscure pinnatinerviis 4-5.5 cm. longis 1.5-2.3 cm. latis; basi cuneatis brevissime petiolatis; pedunculis axillaribus 4 mm. longis puberulis cupulas 2-4 plus minusve racemosas gerentibus. pedicellis vix ullis; cupulis puberulis saepissime 2-partitis, lobo majore obscure 2-3-dentato floram solitariam subtendente; calvee carnoso rugoso turbinato; corolla extus glaberrima 6 mm. longa 5-6 mm. diametro viridescenti-flava, tubo 4 mm. longo subgloboso, lobis 5 ovatodeltoideis acutiusculis 3 mm. longis recurvis; staminibus 5; filamentis omnino corollae adnatis; antheris breviter oblongis albidis; eorum insertionibus pubentibus; ovario fere supero, parte libera ovoidea subcarnosa ruguloso-papillosa; stylo 3.3 mm. longo; stigmate disciformi obscure 3-lobato; fructu ignoto. Uruapan, Michoacan, Mexico, alt. 1525 m., 1 November, 1905, C. G. Pringle, no. 10,123 (type, in hb. Gray). This species differs in its much larger corolla and more lanceolate leaves from the plant of the West Indies and Florida, which has generally passed as S. Schreberi Lam. or S. arborescens R. & S. From S. mexicana DC. (known to the writer only from description) it appears to differ in its leaves, which are often fully twice as long as those described

by DeCandolle and in its decidedly urceolate almost globose rather than cylindric corolla; also in the fact that the corolla-lobes are more than half as long as the tube. S. parcifolia Planch., to judge from Nelson's n. 1836, so identified at the Royal Gardens at Kew, has a much more slender corolla. S. angulata Planch is described by Hemsley, Biol. Cent.-Am. Bot. i. 185, as having flowers only one and one-half lines long and branches angled, while in the present species the branches are terete and even the branchlets are scarcely angled, the flowers being furthermore fully 3 lines long. The genus, however, is much in need of a thorough revision.

Mimosa (§ Habbasia) buceragenia Robinson, n. sp., valde armata 3-5 m. alta; ramulis viridibus albido-costatis puberulis in costis aculeatis; aculeis sparsis recurvatis 4 mm. longis basi albidis compressis 4-5 mm. latis apice brunnescentibus induratis; foliis 10-12 cm. longis 5-6 cm. latis; petiolo et rhachibus et rhachillis breviter molliterque pubescentibus; petiolo 2 cm. longo supra cum glandulo conspicuo oblongo sessili ca. 2 mm. longo instructo subtus cum aculeo saepius uno armato; rhachi aculeis 2-3 parvis instructa; stipulis binis subulatofiliformibus ca. 3 mm. longis erectis; pinnis ca. 11-jugis; foliolis ca. 25-jugis linearibus utrinque viridibus glabris acutiusculis 4-5 mm. longis ca. 0.8 mm. latis saepe leviter falcatis basi valde obliquis: floribus virescentibus spicatis; spicis densis saepissime in axillis binis pedunculatis ca. 4.5 cm. longis 8 mm. diametro; calyce cupulato brevissime 5-dentato; petalis 5 anguste lanceolatis; staminibus 10; ovario stipitato; fructu ignoto. - Valley near Treinte Station, in the vicinity of Cuernavaca, Morelos, Mexico, alt. 1220 m., 26 September, 1905, C. G. Pringle, no. 10,073. A species which, to judge from its inflorescence, belongs in the series Leptostachyae, but well marked in this series by its conspicuous petiolar glands.

Pedilanthus spectabilis Robinson, n. sp., caulibus teretibus crassis foliosis griseis minute granuloso-pulverulis vix 1 m. altitudine; foliis ovato-oblongis brevissime crassiusculeque petiolatis 8-9 cm. longis 4-6 cm. latis integris supra glabriusculis subtus breviter molliterque pubescentibus apice rotundatis saepissime retusis distincte mucronulatis basi breviter cordatis; inflorescentia terminali dichotoma bracteosissima densiuscula ca. 1.6 dm. lata; bracteis late ovatis cordatis sessilibus oppositis integris 4-5 cm. longis et latis internodia valde superantibus acute acuminatis caudato-attenuatis utrinque puberulis rubro-purpureis margine tomentellis; pedicellis griseo-tomentosis; involucro albido 18 mm. longo basi leviter invaginato, labio superiore profunde bipartito, lobis linearibus acutiusculis 6-7 mm. longis quam labio inferiore multo brevioribus margine tomentellis; stipite ovarii

glabro nutanti; filamentis glabris; stylo 1 cm. longo; capsula ca. 1 cm. diametro obtuse 3-lobata subsphaerica; seminibus viridescenti-griseis angulatis 6 mm. longis. — Cañon walls of limerock, Iguala Cañon, near Iguala, Guerrero, Mexico, alt. 760 m., 28 December, 1906, C. G. Pringle, no. 13,914 (type, in hb. Gray). This noteworthy species is probably the most showy of the genus. It differs from P. bracteatus (Jacq.) Boiss. in having pubescent leaves, denser inflorescence, and larger much more caudate-acuminate and strongly colored bracts.

Bonplandia linearis Robinson, n. sp., herbacea ramosa dense caespitosa gracilis 4 dm. vel ultra alta ubique glanduloso-pubescens; ramis erectis vel ascendentibus; foliis alternis anguste linearibus 3-4.5 cm. longis vix 2 mm. latis sessilibus attenuatis cum lobis lateralibus 2 angustis late patentibus instructis; racemis erectis laxifloris 1-1.5 dm. longis; floribus saepissime geminis in pedicellis erectis ca. 1 cm. longis nutantibus; calvee tubuloso 15-striato et venoso-reticulato anthesi 8 fructifero 11 mm. longo leviter curvato paulo nigrescenti, dentibus lanceolato-deltoideis acutis; corolla cyanea ca. 2 cm. longa; tubo gracili ad orem calvois leviter deflexis; lobis anguste obovatis retusis late patentibus ca. 12 mm. longis; filamentis subaequalibus glabris longe exsertis; stylo filiformi glabro, ramis stigmatiferis 3 linearibus papillosis 1.2 mm. longis; ovario ovoideo glabro. — Lava fields, near Coru Station, above Uruapan, Michoacan, Mexico, 26 January, 1907, C. G. Pringle, no. 10,364 (type, in hb. Gray). This species obviously belongs to the hitherto monotypic genus Bonplandia. It differs strikingly from the common B. geministora Cav. in its narrowly linear leaves.

Brittonastrum Barberi Robinson, n. sp., herbaceum 4-6 dm. vel ultra altum; caulibus gracilibus suberectis simplicibus basi rubescentibus alibi pallide viridibus ubique crispe griseo-puberulis; foliis ovato-lanceolatis crenatis obtusis vel superioribus acutis vel etiam subattenuatis 2-3.5 cm. longis 1-2 cm. latis subtus pallidioribus utrinque crispe griseopuberulis superioribus distantibus; petiolis 2-5 mm. longis; inflorescentia anguste paniculata 8-22 cm. longa 5 cm. diametro superne densiuscula; bracteis inferioribus lanceolatis subsessilibus 1-1.5 cm. longis superioribus valde reductis; inflorescentiis secundariis ascendentibus multifloris griseo-puberulis vel -pulverulis inferioribus plus minusve distantibus; bracteolis subulatis minimis et pedicellis purpurascentibus; calvee anguste tubulato anthesi deorsum attenuato fructifero deinde turgido 10-12 mm. longo pulcherrime purpureo grisco-puberulo et atomifero, dentibus lanceolatis parvis acutis erectis 1.5-2 mm. longis; corolla molliter puberula anguste tubulata leviter curvata 2.6 cm. longa, limbo valde ringenti, labio superiore erecto subcucullato inferiore deflexo ca. 2 mm. longo; staminibus juxta labium

superius exsertis. — Near Colonia Garcia in Sierra Madres, Chihuahua, Mexico, alt. 2290 m., 17 July, 1899, C. H. T. Townsend & C. M. Barber, no. 79 (type, in hb. Gray). Previously collected in imperfect specimens at Los Pinitos, Sonora, Mexico, alt. 2000 m., 11 October, 1890, C. V. Hartman, no. 122 (hb. Gray), and in southwestern Chihuahua, August to November, 1885, Dr. E. Palmer, no. FF in part. This species differs from the nearly related B. neo-mexicanum Briq. in its much longer corolla, more pedicellate flowers, shorter petioles, etc., from B. canum (Gray) Briq. in its shorter pedicels, longer less acutely toothed calyx, etc., from B. pullidum (Lindl.) Briq. by its ovate-lance-olate relatively narrower leaves, longer deep crimson calyx, and longer corolla.

Brittonastrum ionocalyx Robinson, n. sp., herbaceum; caulibus quadrangularibus breviter molliterque canescenti-puberulis; foliis deltoideo-ovatis sinu patulo cordatis grosse crenatis obtusis 3-5.5 cm. longis 2.5-4 cm. latis ubique molliter puberulis supra pallide viridibus subtus vix pallidioribus albo-nervosis, petiolo 6-10 mm. longo; inflorescentia 11-17 cm. longa terminali 5-6 cm. diametro densiuscula; bracteis infimis ovatis serrato-dentatis ca. 1 cm. longis, ceteris gradatim minoribus; cymis furcatis compositis minute granuliferis vel glandulosopuberulis; floribus erectis vel paulo nutantibus; calvee cylindrato pulcherrime purpureo griseo-puberulo et atomifero anthesi 1 cm. longo fructifero vix accrescenti dentibus lanceolatis acutis 2 mm. longis erectis nec patulis nec induratis; corolla purpureo-coccinea 2.5 cm. longa leviter curvata externe molliter puberula, faucibus vix dilatatis, limbo ringenti, labio superiore erecto, inferiore pendulo; staminibus sub labio superiore modice exsertis. - Sandia Station, Durango, Mexico, alt, 2288 m., 15 October, 1905, C. G. Pringle, no. 10,146 (type, in lib. Gray). This species differs from B. pallidum (Lindl.) Brig. in its deep purple calyx and much more exserted corolla, as well as in its more compound inflorescence; from B. coccineum (Greene) Brig. in its much shorter calyx-teeth; from B. betonicoides (Lindl.) Briq. in its much shorter petioles; and from the real B. mexicauum (HBK.) Brig. in its very different foliage. To B. ionocalyx should be referred with scarcely a doubt Wright's no. 1532 from mountains east of Santa Cruz, Sonora, which appears to differ only in the fact that the leaves are a trifle less cordate at base.

Brittonastrum Palmeri Robinson, n. sp., herbaceum a basi horizontali radicanti erectum 6-9 dm. altum; caule unico simplici acute quadrangulari saepius flexuoso vel torto ubique breviter crispeque griseo-puberulo; foliis deltoideo-ovatis grosse crenatis acutiusculis vel subacuminatis utrinque griseo-tomentellis vel glabriusculis subtus paulo

pallidioribus 3-6 cm. longis 2.4-3.6 cm. latis basi cordatis; petiolis 4-10 mm. longis; inflorescentia terminali ca. 1.5 dm. longa interrupte spiciformi, verticellastris inferne subremotis superne approximatis densis multifloris, cymulis brevibus densissimis, bracteis inferioribus foliaceis ovatis vel ovato-lanceolatis 2-2.5 cm. longis petiolatis superioribus lanceolatis vel linearibus; pedicellis brevissimis purpureis griseopuberulis, calyce subcylindrato anthesi 1 cm. longo puberulo inferne viridi superne laete purpureo vel violaceo, dentibus argutissimis lineari-lanceolatis ca. 3 mm. longis maturitate subinduratis saepe curvatis plus minusve patentibus; corolla purpurea gracili griseo-puberula apicem versus deorsum curvata 2 cm. longa, labiis brevibus superiore subgaleato; staminibus breviter exsertis. — Alvarez, San Luis Potosi, Mexico, 5-10 September, 1902, Dr. Edward Palmer, no. 53 (type, in hb. Gray), distributed as Cedronella mexicana Benth. Previous collections of what appears to be the same species have been made as follows: Mexico, without precise locality, Sumichrast (hb. Gray), Coulter, no. 1078 (hb. Gray); in mountains near Morales in valley of San Luis Potosi, 1876, Schaffner, no. 682 (hb. Gray); region of San Luis Potosi, 1878, Parry & Palmer, no. 762 (hb. Gray). This species differs clearly from B. mexicanum (HBK.) Briq. in its deltoid-ovate leaves, shorter corolla, etc. It appears to differ in the same respects from B. coccineum (Greene) Brig., known to the writer from description, — a characterization which fails to convince the reader that B. coccineum is distinct from the real B. mexicanum. differs from B. betonicoides (Lindl.) Brig. in its much shorter petioles, longer calvx-teeth, etc.

Brittonastrum Wrightii (Greenman) Robinson, n. comb. Cedronella Wrightii Greenman, Proc. Am. Acad. xli. 244 (1905). The separation of the American simple-leaved species of Cedronella as a new genus Brittonastrum now generally accepted necessitates the transfer of Dr. Greenman's excellent species C. Wrightii.

Russelia Pringlei Robinson, n. sp., caulibus subsimplicibus 1 m. vel ultra longitudine teretibus ca. S-costatis niveo-tomentosis; internodiis 5–6 cm. longis; ramis elongatis gracilibus 4–6-angulatis griseo-tomentosis; foliis oppositis vel ternis inaequalibus lanceolato-ovatis 1.5–2 cm. longis 6–10 mm. latis acutatis basi subcuneatis serrato-dentatis supra viridibus crispe puberulis et squamiferis rugosis subtus pallidioribus densius squamiferis et praesertim in venis nervisque griseo-tomentellis; inflorescentia 3–4 dm. longa 3–4 cm. lata; cymulis oppositis vel ternis; verticellis 3–5 cm. distantibus; pedicellis filiformibus griseo-pubescentibus 3–4 mm. longis; calycis 5 mm. longi lobis ovato-lanceolatis caudato-acuminatis dorso squamiferis; corolla

coccinea tubiformi 16 mm. longa glaberrima, lobis rotundatis 1.5 mm. longis; capsula ovoidea acuminata 6 mm. longa glabra. — On vertical walls of limerock, Iguala Cañon, near Iguala, Guerrero, Mexico, 28 December, 1906, C. G. Pringle, no. 10,367 (type, in hb. Gray). A species peculiar in its terete canescent-tomentose stem.

Stemodia macrantha Robinson, n. sp., suffrutescens 1 m. vel ultra alta; caulibus decumbentibus gracilibus teretibus pubescentibus; ramis saepius simplicibus erectis vel ascendentibus viridibus patenter pilosis 3-6 dm. longis, internodiis 3-10 cm. longis; foliis lanceolato-ovatis utroque angustatis 5-6 cm. longis 2.5-3 cm. latis basi cuneata excepta crenato-serratis supra atroviridibus adpresse pilosis subtus paulo pallidioribus in costis et venis lateralibus pinnatis hirsutulis; petiolis 1 cm. longis hirsutulis superne alatis; inflorescentia terminali 1-4 dm. longa perlaxa folioso-bracteata, pedicellis filiformibus flexuosis glandulosopubescentibus unifloris 2-4 cm. longis ascendentibus ex axillis bractearum saepissime ternis vel quaternis orientibus; calvois laciniis glanduloso-pulverulis et hispidulis lanceolato-linearibus superioribus anthesi usque ad 7 mm. longis infimis paulo brevioribus omnibus a basi gradatim angustatis sed apice vero obtusiusculis; corolla 1.8-2 cm. longis, tubo viridi-flavescenti cylindrato ca. 13 mm. longo 4 mm. diametro purpureo-nervio intus externeque piloso ad fauces distincte sursum curvato, limbo laete purpureo, lobis suborbicularibus subaequalibus apice saepissime retusis; staminibus brevioribus mediae parti tubi affixis 3 mm. longis longioribus paulo supra basin tubi affixis 8 mm. longis omnibus inclusis antheriferis glabris; capsula ovoidea 5 mm. longa atrobrunnea a calvee persistenti circumdata. — Shaded bluffs of the deep barranca, near the foot of the Falls of Tzaráracua, below Uruapan, Michoacan, Mexico, 28 January, 1907, C. G. Pringle, no. 10,356 (type, in hb. Gray). This species is amply distinguished from its Mexican congeners by its much larger flowers, which in fact are decidedly showy for the genus.

Lobelia Nelsonii Fernald, var. fragilis Robinson & Fernald, n. var. a forma typica recedit foliis utrinque viridibus juventate sparse pilosulis mox omnino glabratis lineari-lanceolatis multo brevioribus, maximis ca. 7 cm. longis 8–10 mm. tantum latis. — Mexico, C. G. Pringle, no. 10,360 (type, in hb. Gray). This variety shares with the typical form the soft woody stems and branches as well as-all the more important characteristics of the inflorescence. The varietal name is suggested by the extreme brittleness of the branches, at least when dried. The variety, like the typical form, has numerous showy flowers with bright scarlet corolla. Both plants seem worthy of cultivation.

Piqueria (Subg. Phalacraea) longipetiolata Robinson, n. sp.,

repens subglabra; caule tenui flexuoso prostrato nodis radicante, internodiis saepius perlongis (ad 1 dm.) glabris angulato-costatis; foliis oppositis, limbo late ovato 1.8-3.5 cm. longo 1.2-2.7 cm. lato supra basin integram crenato-dentato supra viridi sparse hispidulo subtus paulo pallidiore glabro basi obtuso vel breviter acuminato apice obtuso, petiolo obcompresso (dorsoventraliter) limbum longitudine aequante: capitulis parvis ca. 9-floris cymosis, cymis ca. 7-13-capituliferis terminalibus; involucri campanulati squamis ca. 6 obovatis viridibus obtusis ciliatis 3 mm. longis; corollae tubo proprio brevi glanduloso-puberulo, faucibus campanulatis quam tubo longioribus subglabris, limbi dentibus 5 late ovatis obtusis; achaeniis immaturis sursum hispidulis basi rectiusculis. — Colombia, near R. Flautas, R. Paez Valley, Tierra Adentro, Central Cordillera, alt. 2900 m., 26 January, 1906, H. Pittier, no. 1208 (hb. U. S. Nat. Mus.; fragment in hb. Gray). This species stands nearest P. callitricha Robinson, Proc. Am. Acad. xlii. 15 (1906), but differs in having smaller more coarsely and simply toothed leaves with much longer petioles. It is also a smoother plant and has fewerflowered heads.

Stevia alatipes Robinson, n. sp., herbacea perennis ca. 1 cm. alta hirsuta; radice fibrosa; foliis radicalibus ovatis vel obovatis crenatoserratis ca. 8 cm. longis 4-5 cm. latis pinnatinerviis utrinque hirsutis haud vel vix punctatis apice rotundatis basi angustatis in petiolum alatum decurrentibus; foliis caulinis oppositis 2-4-jugis oblanceolatis vel fere spatulatis in petiolum alatum basi attenuatis; inflorescentia laxissime pauciramosa; ramis nudiusculis, capitula pauca parva sacpe aggregata ferentibus; bracteis 7 mm. longis lanceolatis sessilibus herbaceis; pedicellis ad 1 cm. longis filiformibus glanduloso-puberulis; eapitulis ea. 12 mm. longis 4-floris; involueri squamis 5 viridibus lanceolato-linearibus acutis inaequalibus ca. 7 mm. longis; corollis 7 mm. longis, tubo viridescenti puberulo, limbo albo; achaeniis nigrescentibus 3.2 mm. longis minute puberulis; pappo e squamis 3 brevibus albis et aristis 3 albidis 5-6 mm. longis barbellatis composito. — Pine forests. Uruapan, Michoacan, Mexico, alt. 1680 m., 14 November, 1905, C. G. Pringle, no. 10,124 (type, in hb. Gray). Near S. elatior HBK. but readily separable by its much larger basal leaves with long-attenuate base, its aggregated heads, etc.

Stevia Lozanoi Robinson, n. sp., caule tereti purpureo pilis crispis griseis brevibus pubescenti supra laxe ramoso folioso; ramis divergenti-ascendentibus subsimplicibus gracilibus ca. 1 dm. longis foliosis in corymbos subdensos capitiformis terminantibus; foliis inferioribus ignotis, superioribus linearibus sessilibus alternis integris 4–5 cm. longis 3–7 mm. latis utrinque obscure viridibus punctatis 1–3-nerviis sparse

pubescentibus margine saepe purpurascenti-hispidulis apice obtusis basi attenuatis; corymbis 3-4 cm. diametro convexis 10-20-capitulatis; capitulis 1.5 cm. longis breviter pedicellatis vel etiam sessilibus, bracteis linearibus 3-6 mm. longis herbaceis; squamis involucri ca. 6 linearibus acutis purpureis 7 mm. longis pilis crispis atomisque resinosis tectis; flosculis 5; corollis 8 mm. longis, tubo purpureo pubescenti gradatim a basi sursum leviter ampliato, limbo albo patenti 5-lobo, lobis oblongis obtusiusculis; achaeniis gracilibus 5 mm. longis sursum praesertim in angulis hispidulis; pappo e squamulis 5 albidis brevissimis et aristis 5 purpureis divergentibus scabratis composito. — Sandia Station in mountains of northwest Durango, Mexico, alt. 2290 m., 12 October, 1905. C. G. Pringle, no. 10,092 (type, in hb. Gray). A species evidently related to S. laxiftora DC. and S. serrata DC., but readily distinguished by its numerous separate dense corymbs and entire leaves. Named for Sr. Filemon L. Lozano, faithful and efficient companion and assistant of Mr. Pringle in his recent journeys to Mexico.

Stevia Plummerae Gray, var. durangensis Robinson, n. var., foliis tenuibus lanceolato-oblongis 6-9 cm. longis 1.5-2 cm. latis supra mediam partem serratis nec dentatis supra pilis brevissimis crispis griseo-puberulis subtus molliter pubescentibus; corollis albis. — Barranca below Sandia Station, Durango, Mexico, alt. 2135 m., 13 October, 1905, C. G. Pringle, no. 10,106 (type, in hb. Gray). Nearer var. alba Gray, Syn. Fl. i. pt. 2, 92, than to the typical form, but differing in its thinner larger less strongly reticulated and much more pubescent leaves.

Eupatorium acutidentatum Robinson, n. sp., herbaceum erectum 6 dm. altum; caule gracili tereti striato viridi vel purpurascenti crispe puberulo subsimplici vel modice oppositirameo; foliis oppositis ovatolanceolatis tenuibus argute serrato-dentatis basi cuneata et apice attenuato integris a basi 3-5-nerviis 3.6-5 cm. longis 1.8-2.2 cm. latis supra laete viridibus scabriusculis subtus vix pallidioribus in nerviis sparse pubescentibus, petiolo puberulo ca. 5 mm. longo; capitulis ca. 12-floris 1 cm. longis numerosis graciliter pedicellatis in corymbos valde convexos collectis, pedicellis 5-8 mm. longis griseo-puberulis; involncri squamis anguste oblongis vel lanceolatis attenuatis herbaceis griseo-puberulis inaequalibus laxe imbricatis interioribus quam flosculis dimidio brevioribus; corollis albis glabris, tubo proprio gracili quam faucibus gradatim sed valde ampliatis distincte breviore; achaeniis nigrescentibus 3 mm. longis prismaticis deorsum paululo angustatis sursum hispidulis; pappi setis minute barbellatis corolla fere aequilongis basin versus roseis. — Barranca below Sandia Station, Durango, Mexico, alt. 2135 m., 15 October, 1905, C. G. Pringle, no. 10,095 (type, in hb. Gray). This species is obviously close to E. betulaefolium

(Greene) Robinson, n. comb. (Kyrstenia betulaefolia Greene, Leafl. i. 10, 1903.) It differs, however, in having decidedly narrower leaves, which are entire at the attenuate apex; the bracts are also of different form, being narrowly lanceolate, quite entire, and strongly attenuate; furthermore the involucral scales are of a more herbaceous texture. Whether these distinctions will prove constant cannot be foretold; but on the whole they appear rather too significant to permit the placing of the present plant under E. betuluefolium as a variety.

Eupatorium campechense Robinson, n. sp., subglabrum; ramis teretibus striatulis glaberrimis lignescentibus modice medullosis; foliis oppositis petiolatis lanceolatis attenuatis saepe falcatis 3-nerviis crassiusculis nitidulis 8-10 cm. longis 2.4-3 cm. latis glabris vel in nerviis primariis obscure puberulis subremote serratis; petiolo ca. 1 cm. longo obcompresso supra canaliculato glabro vel papilloso; inflorescentiis amplis oppositirameis: capitulis numerosis ca. 5-floris graciliter pedicellatis subdense corymbosis; ramulis paniculae et pedicellis gracillimis puberulis: involucri squamis 5-stachvis imbricatis stramineis glaberrimis obtusis, extimis brevissimis ovatis ca. 1 mm. longis intermediis gradatim longioribus ovato-oblongis, intimis (numero ca. 5) anguste oblongis 7 mm. longis; corollis tubulosis sine faucibus distinctis 6 mm. longis, dentibus limbi ca 1 mm. longis lanceolatis recurvatis; achaeniis prismaticis 5-angulatis fuscis in faciebus et in costis pubescentibus 3.3 mm. longis deorsum modice angustatis; pappi setis ca. 20 levibus albidis 4-5 mm. longis. — Apazoli near Yohaltun, Campeche, Mexico, 30 December, 1900, E. A. Goldman, no. 504 (type, in hb. U. S. Nat. Mus.; fragments in hb. Gray). A species well marked and apparently without close ally.

Eupatorium chrysostyloides Robinson, n. sp., herbaceum suberectum 1.3-4 dm. altum pilis crispis griseis brevibus hinc inde glanduliferis puberulum; caule solitario modice curvato vel flexuoso obtuse angulato pallide viridi folioso, in parte inferiore subsimplici; foliis oppositis longe petiolatis concoloribus viridibus nec lucidis late deltoideo-ovatis 3-6 cm. longis 2.4-5 cm. latis obtusis vel modice acutis grosse crenato-dentatis basi subtruncatis 3-nerviis in petiolum breviter decurrentibus; petiolo 1-4.5 cm. longo; corymbis rotundatis multicapitulatis densiusculis ramos terminantibus; pedicellis filiformibus griseo-pubescentibus; capitulis ca. 20-floris ca. 1 cm. longis 6 mm. diametro; involucri turbinato-cylindrati squamis numerosis anguste lanceolatis viridibus pallide nervatis hispidulis acutissimis valde inaequalibus multiseriatis; corollis viridi-albidis angustissimis brevissime 5-dentatis, faucibus nullo modo ampliatis; styli ramis longissimis aureis valde exsertis; achaeniis 5-angulatis prismaticis 2.5 mm. longis basi

angustatis albo-callosis sursum paulo hispidulis, pappi setis ca. 25 lacte albis minute barbellatis. — On limerock, Sierra Madre, above Monterey, Mexico, alt. 915 m., 27 April, 1906, C. G. Pringle, no. 10,231 (type, in hb. Gray). This species belongs to a small but increasing group of very nearly related plants, including E. Parryi Gray, E. chrysostylum Robinson, and E. sphenopodum Robinson. From all these species, the present one differs in its exceedingly short crisped pubescence.

Eupatorium durangense Robinson, n. sp., herbaceum 6-9 dm. altum; caule tereti oppositirameo folioso purpurascenti ubique minuteque crispo-puberulo; foliis oppositis ovatis deflexis breviter petiolatis firmiusculis obtusis vel vix acutis paulo supra basin 3-5-nerviis supra viridibus pilosellis subtus vix pallidioribus leviter reticulatovenosis in nervis venisque sparse pubescentibus serratis 2-3 cm. longis 1.3-2.2 cm. latis scabrido-ciliolatis, petiolo puberulo supra concavo 2-3 mm. longo; capitulis ca. 12-floris numerosis in corymbis convexis terminalibus collectis, pedicellis 5-12 mm. longis filiformibus griseopuberulis; involucri squamis pallide viridibus griseo-puberulis oblongolinearibus acutis valde inaequalibus sed laxe imbricatis interioribus ca. 4-5 mm. longis; corollis albis 6-7 mm. longis, tubo proprio gracili fauces gradatim sed distincte ampliatos subcylindratos subaequanti; achaeniis nigris gracilibus 5-angulatis in angulis sursum hispidulis; pappi setis simplicibus corollam aequantibus superne laete albis basin versus roseis. — Barranca below Sandia Station, Durango, Mexico, alt. 2135 m., 15 October, 1905, C. G. Pringle, no. 10,096 (type, in hb. Gray).

Var. angustius Robinson, n. var., foliis angustioribus ovato-lanceolatis attenuatis maximis 3.2 cm. longis 1.7 cm. latis supremis saepe alternantibus. — Mesa de Sandia, northwestern Durango, Mexico, alt. 2745 m., 14 October, 1905, C. G. Pringle, no. 10,097 (type, in hb. Gray). This variety has something the appearance of E. Robinsonianum Greene, but may be readily distinguished by its more herbaceous involucre, thickish more pubescent and regularly deflexed leaves, shorter stouter petioles, etc.

Eupatorium erythrocomum Robinson, n. sp., suffrutescens laxe procumbens; caulibus tenuibus teretibus arcuatis ramosis atropurpureis striatulis plerumque ca. 2 mm. diametro cum pilis moniliformibus adpresse villosulis; foliis oppositis ovatis vel ovato-lanceolatis breviter petiolatis, limbo 2–2.8 cm. longo 1–1.2 cm. lato supra basin subrotundatam integram argute serrato apice acuto 3-nervio supra viridi glabriusculo subtus saepissime purpurascenti praesertim in nervis venisque adpresse pilosis, petiolo tereti purpureo ca. 2 mm. longo, venis supra

impressis, dentibus limbi utroque ca. 5; capitulis ca. 30-floris paucis 4-11 in corymbo terminali, pedicellis ca. 1 cm. longis erectis vel ascendentibus subfiliformibus atropurpureis adpresse villosulis, bracteis linearibus; involucri campanulati squamis ca. 15 lanceolati-linearibus subaequalibus vix imbricatis obtusis vel acutiusculis pilosis ca. 5 mm. longis margine praesertim apicem versus pulcherrime ciliatis; corollis albis 4 mm. longis, tubo proprio gracili fauces ampliatos subcylindratos subaequanti, dentibus limbi 5 acutiusculis hispido-pilosis; achaeniis prismaticis praesertim in angulis breviter hispidulis; pappi setis pulcherrime roseis. - Steep rocks, Ixtaccihuatl, Mexico, alt. 2440 m., January, 1906, C. A. Purpus, no. 1578 (type, in hb. Gray). This attractive species of Eupatorium was submitted to the writer by Mr. T. S. Brandegee. It approaches E. prunellifolium HBK., but differs in its slender flexuous procumbent stems, and more evenly and sharply serrate leaves, which are essentially glabrous above. E. oligocephalum DC., an imperfectly known species, may also be of this affinity; but it is described as having glabrous involucral scales.

Eupatorium hospitale Robinson, n. sp., arboreum : ramis 6-angulatis striatis molliter lignosis medullosis glabris; foliis oppositis lanceolato-oblongis serratis vel subintegris petiolatis penninerviis utrinque glabris crassis siccitate nigrescentibus pellucide punctatis lineolatisque caudato-acuminatis basi attenuatis 16-18 cm. longis 5-6 cm. latis: panicula terminali pyramidata oppositiramea patenter ramosa obsolete pilosiuscula vel glabra multicapitulata; capitulis in summis partibus ramulorum sessilibus parvis ca. 6-floris; squamis involucri valde inaequalibus, interioribus oblongis obtusis 5 mm. longis paucis caducissimis, exterioribus multo brevioribus imbricatis dorso margineque pilosiusculis apice rotundatis persistentibus aetate patentibus; flosculis vero similiter albidis vel viridescentibus; corollis 4 mm. longis, tubo proprio gracili, faucibus cylindratis saepius vix ampliatis; achaeniis ca. 3 mm. longis brunneis acute 5-angulatis basi attenuatis in faciebus concavis pilosis ad angulos etiam hispidulis; pappi setis sordidis ca. 35 corollam subaequantibus. — E. vanillosmoides Hemsl., Biol. Cent.-Am. Bot. ii. 102 (1881), not Sch. Bip. ex Bak. in Mart. Fl. Bras. vi. pt. 2, p. 346 (1876). — Mirador, Vera Cruz, Mexico, Liebmanu, no. 43 (type, in hb. Gray), Sartorius (hb. Gray); Orizaba, Mexico, October, 1855. Schaffner (hb. Gray), Botteri, no. 613 (hb. Gray). marked species appears never to have been described. The plant in question has been repeatedly distributed as Eupatorium vanillosmoides Sch. Bip., but the species to which Schultz really gave this name was a Brazilian plant of entirely different affinity, referred by Mr. Baker (Fl. Bras. vi. pt. 2, p. 346) to the synonymy of E. pyrifolium DC.

is true Schultz well knew the Mexican plant, and ascribed to it the same specific name (vanillosmoides), but under another generic name. In describing this hitherto uncharacterized Mexican plant it seems unwise to take up the nomen nudum E. vanillosmoides Hemsl., a name inadvertently ascribed by Mr. Hemsley to Schultz, although, as we have seen, Schultz used this binominal combination for quite a different plant of Brazil. To avoid probable confusion the Mexican plant is herewith given a new and distinctive name. The designation chosen is suggested by the fact that some of the internodes below the inflorescence are often swollen, hollowed, and provided with a somewhat regular rounded ingress for small insects, probably ants. These enlargements are not always present, and are doubtless of the nature of galls developing through insect irritation, and later serving as nesting places for the insects.

Eupatorium hymenolepis Robinson, n. sp., gracile patente ramosum; caule tereti nigrescenti obsolete strigilloso; ramis gracillimis flexuosis; foliis oppositis longe petiolatis ovatis vel rhomboideis basi abrupte angustata acuta excepta grosse serratis apice caudato-attenuatis 6-7.5 cm. longis 2-3.5 cm. latis tenuibus utrinque viridibus in nervis adpresse pilosiuseulis subtus haud pallidioribus supra sparse strigillosis; cymis parvis 6-10-capitulatis graeiliter peduneulatis saepissime nutantibus : capitulis parvis 3.5 mm. longis ca. 18-floris ; involucri companulati squamis valde inaequalibus albo-scareosis in media parte tantum viridi-striatis, interioribus lineari-oblongis obtusissimis, exterioribus brevioribus acutis vel acuminatis: corollis albis 2.5 mm. longis glabris basin versus modice angustatis; dentibus 5 ovato-deltoideis brevibus patentibus; styli ramis albis paulo clavellatis; achaeniis nigris 5-angulatis 1.3 mm. longis basi albo-callosis sursum minute hispidulis, costis albidis; pappi setis gracillimis ca. 20 corolla distincte brevioribus. — Falls of Tzararacua, near Uruapan, Mexico, 28 January, 1907, C. G. Pringle, no. 10,355 (type, in hb. Gray). somewhat resembles E. hymenophyllum Klatt, but has slightly firmer leaves 3-nerved from the very base instead of from a point somewhat above the base: it differs also in its involucre. From E. Gonzalezii Robinson, to which it also bears some resemblance, it may be readily distinguished by its more attenuate leaves and scarious involucral scales.

Eupatorium isolepis Robinson, n. sp., suffruticosum; caulibus teretibus flexuosis oppositirameis brunneo-purpureis pubescentibus, pilis moniliformibus transverse purpureo-striatis; foliis oppositis graciliter petiolatis ovatis acuminatis serratis tenuibus subpellueidis subconcoloribus supra glabris subtus in nervis sparse pilosis penninerviis basi

rotundatis paululo in petiolum saepe subdecurrentibus 3-6.5 cm. longis 1.6-4 cm. latis; petiolo 1-4 cm. longo subtus convexo subglabro supra canaliculato villoso; capitulis 9 mm. longis 6 mm. diametro 20-floris numerosis ad apices ramorum glomerato-aggregatis, corymbis rotundatis densiusculis ca. 4 cm. diametro; pedicellis filiformibus puberulis 2-6 mm. longis; involucri campanulati squamis ca. 10 elliptico- vel obovato-oblongis aequilongis apice rotundatis saepius pulcherrime ciliatis dorso pubescentibus 3.2 mm. longis 1.5 mm. latis pallide viridibus; corollis albis, tubo proprio gracili 2 mm. longo glabro, faucibus campanulatis glabris, dentibus limbi 5 deltoideis pilosiusculis; antheris vix connatis apice longe appendiculatis; achaeniis nigrescentibus 5angulatis 1.5 mm. longis sursum praesertim in angulis hispidulis apice cupula albida coronatis; pappi setis capillaribus vix barbellatis laete albis vel saepissime pulcherrime roseis corollam fere aequantibus caducis. — Open moist places, rocks of barranca, Ixtaccihuatl, Mexico, alt. 2440 m., C. A. Purpus, no. 1496 (type, in hb. Gray); also in the Valley of Mexico, Schaffner, no. 201 (hb. Gray). This species differs from E. pazemarense HBK, in its very obtuse involucral scales; from E. photinum Robinson, in its thin pubescent less attenuate leaves. It is perhaps most nearly related to E. Schaffneri Gray, but it differs from that species in its more attenuate-acuminate and more regularly serrate leaves which are pinnately veined, while in E. Schaffneri they are palmately nerved from the very base.

Eupatorium phoenicolepis Robinson, var. guatemalensis Robinson, n. var., foliis quam eis formae typicae multo majoribus 12–14 cm. longis 9–10 cm. latis tenuioribus cordatis supra scabriusculis subtus in nervis venisque laxiuscule pubescentibus nec tomentosis; involucri squamis et floribus necnon achaeniis formae typicae simillimis. — Vol. Atitlan, Department of Solalá, Guatemala, alt. 2500–2700 m., 16 February, 1906, W. A. Kellerman, no. 5199 (type, in hb. Field Museum of Natural History; fragment in hb. Gray); between Patahil and San Lucas, Department of Solalá, Guatemala, 15 February, 1906, W. A. Kellerman, no. 5194 (hb. Field Mus.).

Eupatorium saltillense Robinson, n. sp., fruticosum 9-15 dm. altum oppositirameum; ramis teretibus late patentibus arcuato-ascendentibus a cortice brunneo-griseo obtectis foliosis; foliis ovatis tenuibus translucentibus integris vel obsolete serratis vel plus minusve distincte serrato-dentatis vix discoloribus supra sparse pilosulis obscurissime punctatis vel omnino epunctatis subtus minute glanduloso-punctatis et praesertim in nervis venisque puberulis apice obtusis vel obtusiusculis numquam attenuatis basi angustatis in petiolo decurrentibus et margine saepissime revolutis, limbo 4-5.8 cm. longis 2.3-3.3 cm. lat.s, nervis

subtus albidis prominulis, venis lateralibus utrinque ca. 5 inaequidistantibus maximis supra basin orientibus; petiolis 5-8 mm. longis leviter marginatis basi linea transversa connexis; inflorescentiis corymbosis valde convexis oppositirameis multicapitulatis; bracteis inferioribus petiolatis ovatis foliis similibus sed multo minoribus superioribus anguste linearibus sessilibus; pedicellis rectis filiformibus patentiascendentibus pilis crispis obtectis; capitulis parvis numerosissimis saepissime 5-floris 8 min. longis; squamis involucri ca. 8 linearibus vix imbricatis sordide puberulis acutiusculis interioribus 4-5 mm. longis extimis 1-3 multo brevioribus; corollis glabriusculis 4.6 mm. longis albidis vel roseis, tubo proprio gracili quam faucibus subcylindratis breviore, dentibus limbi ovato-deltoideis; achaeniis nigris prismaticis griseo-puberulis 3 mm. longis; pappi setis praesertim basi pulcherrime roseis corollam vix acquantibus. — Mountains near Saltillo, Coahuila, Mexico, alt. 2135 m., 5 October, 1905, C. G. Pringle, no. 10,080 (type, in hb. Gray). This species is obviously related to E. micranthum Less. It differs, however, in many small characters. The leaves are thin and translucent while in E. micranthum they are thickish and quite opaque. In E. saltillense they are also much broader relatively to their length and not attenuate. The nervation is furthermore quite different, for in E. micranthum the lateral veins leave the midnerve in a pretty regular pinnate fashion, while in E. saltillense they are less numerous and less regular and give the leaves somewhat the appearance of being 3nerved from a point above the base.

Eupatorium sexangulare (Klatt) Robinson, n. comb. Piptocarpha sexangularis Klatt, Botanisches Beiblatt zur Leopoldina, 1895, p. 1. Mr. H. A. Gleason, during a recent examination of the Vernonicue in the Gray Herbarium, called my attention to the type of Dr. Klatt's Piptocarpha sexangularis, which appeared wholly irreconcilable with the genus in which it had been placed and indeed with any other genus of the Vernonieae. Unfortunately the specimen, although showing well the stem, leaves, inflorescence, involucral scales, etc., has but very few flowers, and these have been so damaged by decay or insects that it is impossible to state precisely the form of the anthers or style-tips; nevertheless there can be no doubt that the plant is a Eupatorium, and as it appears to be unlike any species previously referred to that genus, it may be simply transferred thither. In its sharply angled stem and large thickish lanceolate leaves it bears considerable resemblance to the plant here described as E. hospitale. It may be readily distinguished, however, by the different venation of the leaves, entirely glabrous achenes, etc.

Eupatorium sphenopodum Robinson, n. sp., herbaceum oppositi-

rameum molliter hirsutum, pilis longis patentibus plus minusve moniliformibus albis viscidulis inaequalibus; foliis oppositis deltoideis vel ovato-deltoideis longe petiolatis late cordatis grosse duplicateque crenato-dentatis tenuibus utrinque praesertim subtus in nervis pubescentibus, limbo 11-12 cm. longo 8-10 cm. lato, petiolo sursum alato ca. 7 cm. longo hirsuto; panicula oppositiramea; capitulis ca. 11-floris 10-11 mm. longis 4-5 mm. diametro; pedicellis gracilibus rectis valde inaequalibus 2-12 mm. longis; involucri squamis lanceolatis attenuatis peracutis 3-4-seriatis valde imbricatis viridibus albo-nerviis hispidulis adpressis: corollis angustissime tubulosis 3.5 mm. longis viridiscenti-albidis, faucibus vix ullis; dentibus limbi brevissimis erectis; styli ramis valde exsertis aurantiacis vel maturitate brunnescentibus valde clavatis: achaeniis fuscis prismaticis 2.7 mm. longis deorsum modice angustatis basi callosis plus minusve curvatis in faciebus et in costis sursum hispidulis; pappi setis inaequalibus ca. 20 vix scabratis laete albis corollam fere aequantibus. — On shaded cliffs of limerock, Sierra Madre. above Monterey, Mexico, 1000 m. alt., 16 July, 1906, C. G. Pringle, no. 10,259 (type, in hb. Gray). This species is closely related on the one hand to E. chrysostylum Robinson and on the other to E. Parryi Grav. From the former it differs in its more slender freely branched less pubescent stems, large bluntly toothed leaves and much longer pedicels. From E. Parvyi it differs in having much larger leaves (of which even the uppermost are opposite), winged petioles, and smaller fewerflowered heads.

Eupatorium thyrsiflorum (Greene) Robinson, n. comb. Kyrstenia thyrsiflora Greene, Leafl. i. 9 (1903). The genus Kyrstenia Neck. does not seem to the writer in any way satisfactorily separable from Eupatorium. When all species are duly considered the two groups appear to merge by imperceptible gradations. There seems, however, to be little doubt that Professor Greene's K. thyrsiflora is specifically distinct and may be appropriately transferred to the older genus. From the more typical material of the species, with leaves in varying degree toothed and somewhat narrowed at the base, the following plant may be varietally separated.

Var. holoclerum Robinson, n. var., foliis ovatis integris vel obsolete crenato-serratis basi fere rotundatis. — Near the city of Durango, Mexico, April to November, 1896, *Dr. E. Palmer*, no. 755 (type, in hb. Gray). Distributed as *E. occidentale*, var. arizonicum Gray.

Eupatorium triangulatum Alam. ex DC. Prod. v. 172 (1836). After a careful examination of the types of this species in the DeCandollean herbarium at Geneva, and of E. rubricaule HBK. at the Museum of Natural History at Paris, the writer can find no differences of moment.

DeCandolle does not appear to have seen the plant of Humboldt and Bonpland, and the distinctions on which he attempted to separate *E. triangulatum* were deduced from the description of Kunth, but on comparison of the plants themselves these distinctions do not appear to be definite or important. The species should certainly be united and stand under the older name E. RUBRICAULE HBK.

Brickellia Betonicaefolia Gray, Pl. Wright. ii. 72 (1853). In the typical form of this rather variable species the leaves are ovate-oblong and flat, the larger 6 cm. long, 3 cm. wide; petioles very short, scarcely over 2 mm. long; longer scales of the involucre rather attenuate.

Var. HUMILIS Gray, l. c. Leaves ovate-oblong, flat, essentially sessile, the largest 3.8 cm. long, 1.5 cm. wide; longer scales of the involucre linear, attenuate.

Var. elliptica Robinson, n. var., foliis late ellipticis planis 3-4 cm. longis 1.8-3 cm. latis subsessilibus; squamis involucri atropurpureis interioribus lanceolati-linearibus attenuatis. — Barranca below Sandia Station, Durango, Mexico, alt. 2135 m., 13 October, 1905, C. G. Pringle, no. 10,102 (type, in hb. Gray).

Var. conduplicata Robinson, n. var., caule 6-9 dm. alto; foliis 2-3 cm. longis 1.4-1.8 cm. latis saepissime conduplicatis; petiolo gracile 4-5 mm. longo; squamis involucri interioribus oblongi-linearibus atropurpureis vix attenuatis. — San Luis Potosi, Mexico, on rocky hills, San José Pass, 16 August, 1890, C. G. Pringle, no. 3171 (distributed as B. betonicaefolia Gray?). Mountains near General Cepeda, Coahuila, Mexico, alt. 1920 m., 7 October, 1905, C. G. Pringle, no. 10,081 (type, in hb. Gray).

Brickellia saltillensis Robinson, n. sp., caulibus teretibus 9-12 dm. altis gracilibus striatulis pallide viridibus vel leviter purpurascentibus molliter breviterque pubescentibus foliosis; foliis alternis petiolatis in axillis proliferis, laminis late ovatis obtusis vel subacutis serratis tenuibus utrinque viridibus brevissime pubescentibus basi rotundatis 4-5.5 cm. longis 2-4 cm. latis a basi 3-nerviis laxe reticulato-venosis; petiolo 1-1.4 cm. longo pilis crispis glanduloso-puberulo; foliis parvis ellipticis 2-4 in axillis; panicula angusta 7-30 cm. longa 4-7 cm. diametro folioso-bracteata; cymulis saepissime 3-capitulatis; pedicellis gracillimis filiformibus glanduloso-puberulis nutantibus; capitulis ca. 14-floris 1.8 cm. longis; involucri subturbinati squamis exterioribus viridibus striatis lanceolatis attenuatis dorso puberulis, interioribus lanceolati-linearibus attenuatis purpureo-tinctis 1-1.2 cm. longis; corollis albidis angustissime tubulosis 8-9 mm. longis glabris, faucibus nullis, limbi dentibus brevissimis erectis; styli ramis nigrescentibus vix clavatis longe exsertis; achaeniis columnaribus 4.5 mm. longis adpresse pubescentibus fuscis basi callosis, pappi setis ca. 22 aequalibus tenuibus laete albis 5 mm. longis vix scabratis. — On mountains, Saltillo, Mexico, alt. 2135 m., 5 October, 1905, C. G. Pringle, no. 10,082 (type, in hb. Gray).

Lagascea helianthifolia HBK., var. adenocaulis Robinson, n. var., caule (3-4 m. alto) usque ad summam partem dense glanduloso-puberulo nec piloso; foliis longiuscule oblanceolato-oblongis attenuatis supra scabris subtus paulo pallidioribus molliter tomentellis. — Hedgerows, Uruapan, Michoacan, Mexico, 24 January, 1907, C. G. Pringle, no. 13,907 (type, in hb. Gray). A transition between this variety and the typical spreading-pilose form is shown by L. C. Smith's no. 964 from the mountains of San Juan del Estado, Oaxaca.

Lagascea helianthifolia HBK., var. levior Robinson, n. comb. *Nocca helianthifolia* Cass., var. *levior* Robinson, Proc. Am. Acad. xxxvi. 468 (1901).

Lagascea helianthifolia HBK., var. suaveolens Robinson, n. comb. L. suaveolens HBK. Nov. Gen. et Spec. iv. 25 (1820). Nocca helianthifolia Cass., var. suaveolens Robinson, l. c.

Lagascea Palmeri Robinson, n. comb. *Nocca Palmeri* Robinson, l. c. 471 (1901).

Lagascea Pringlei Robinson, n. comb. *Nocca Pringlei* Robinson, l. c. 469 (1901).

Guardiola Palmeri Robinson, n. sp., glaberrima atroviridis compacte ramosa foliosa 3.5 dm. alta basi lignescens; caulibus teretibus striatulis gracilibus, ramis oppositis ascendentibus; foliis oppositis petiolatis ovatis vel subreniformibus integerrimis vel plus minusve repandis nec angulatis nec dentatis 1.5-3 cm. longis 1.2-2.8 cm. latis utringue leviter reticulato-venosis subtus vix pallidioribus apice rotundatis basi late cordatis, petiolo 5-7 mm. longo; inflorescentiis in apicibus ramorum folioso-bracteosis 1-3-capitulatis; pedicellis 3-7 mm. longis; capitulis 12-14 mm. longis 6-8 mm. diametro; involucri subevlindrati fusco-viridis 1 cm. longi 4-5 mm. crassi squamis oblongis obtusiusculis striatulis leviter convexis nullo modo carinatis; radiis ca. 3; corollae tubo gracili glaberrimo 5 mm. longo, ligula elliptica 4 mm, longa 2.2 mm. lata bidentata alba; achaeniis immaturis concavo-convexis obovato-oblongis 4.6 mm. longis glabris; floribus disci ca. 10 gracillimis, tubo corollae ca. 9 mm. longo, faucibus brevissimis campanulatis, lobis limbi 5 lineari-oblongis obtusis recurvatis albis; filamentis albis tomentosis quam antherae virides multo brevioribus. — Outer circle of mesas, Otinapa, Durango, Mexico, alt. about 2450 m., 25 July-5 August, 1906, Dr. E. Palmer, no. 377 (type, in hb. Gray). This species in its few scattered heads, broad clearly petiolate leaves, and unkeeled involucral scales, closely approaches G. Rosei Robinson;

but it differs from that species in its decidedly smaller untoothed leaves, which are rounded at the apex.

Zinnia tenella Robinson, n. sp., erecta gracilis annua tenuiter pilis subappressis griseis in novellis copiose pubescens in parte inferiore simplex supra saepissime 3-5-ramea 1.5-2.7 dm. alta; foliis tenuibus lanceolatis integris utrinque viridibus appresso-puberulis et sparse atomiferis obtusiusculis 3-nerviis patentibus vel deflexis basi cuneatis brevissime petiolatis 1.5-3.5 cm. longis 4-10 mm. latis; capitulis saepissime 1-5 terminalibus graciliter pedunculatis erectis ca. 7 mm. diametro (ligulis exclusis) aequi-altis; involucri campanulati squamis paucis (ca. 8) late oblongis obtusissimis subaequalibus appressis tenuiter appresso-puberulis ca. 5 mm. longis; ligulis ca. 5 patentibus late oblongis aurantiacis extus prope apicem saepe viridi-striatulis vel reticulatis minutissime puberulis et granuliferis 7.5 mm. longis 5-6.5 mm. latis; achaeniis florum liguliferorum obovatis concavo-convexis margine ciliatis in summa parte bidentatis 4 mm. longis (immaturis); corollis florum (ca. 15) disci 3 mm. longis sursum leviter ampliatis infra limbum brevissimum aurantiacum plus minusve purpureo-lineatis; paleis tenuibus ovato-oblongis acutis carinatis ciliolatis apice saepissime aurantiacis; achaeniis obovatis. - Very common on grassy plains and hills, Tejamén, Durango, Mexico, alt. about 2135 m., 21-27 August, 1906, Dr. E. Palmer, no. 500 (type, in hb. Gray). This species resembles in many respects Z. linearis Benth. It differs, however, in having broader leaves and a more slender erect and simple habit. It is especially to be distinguished from the related species by its fewer subequal involucral scales.

Cymophora Robinson, n. gen., Compositarum Helianthiearum. Capitula homogama parva cymosa; disco parvo leviter convexo; paleis lanceolato-oblongis acutis carinatis flosculos amplectentibus. Involucrum anguste campanulatum, squamis paucis ovato-oblongis obtusis saepe mucronulatis subherbaceis striatis subaequalibus. Corollae tubulosae, tubo proprio brevissimo, faucibus cylindratis, limbo vel aequaliter 5-dentato vel flosculorum exteriorum plus minusve irregulari sed vix radiatiformi. Antherae connatae basi obtusae vel obscure sagittato-auriculatae apice distincte appendiculatae. Styli rami breves recurvato-patentes filiformes graciliter et distincte appendiculati, appendicibus capillaribus rectis ca. 0.1 mm. longis. Achaenia anguste obconica pilis curvatis longiusculis albis villosa, pappo nullo. — Herba annua pubescens et glandulifera; foliis oppositis late ovatis subintegris; corollis albis; antheris purpureis.

C. Pringlei Robinson, n. sp., caulibus laxe oppositeque ramosis patente pilosis 3-4 dm. altis; ramis arcuato-curvatis vel flexuosis

teretibus; foliis tenuibus a basi 3-nerviis breviter petiolatis, limbo late ovato integerrimo vel obsolete repando obtusiusculo 2-6 cm. longo 1.6-4 cm. lato utrinque sparse adpresseque pilosis supra viridi subtus pallidiore basi obtuso saepissime obliquo; cymis compositis laxis glanduloso-pubescentibus; capitulis ca. 10-floris 7 mm. longis 3.5 mm. diametro; pedicellis filiformibus rectis glanduloso-puberulis 6-10 mm. longis; involucri squamis ca. 6 subaequalibus (una vel duabus extimis valde minoribus exceptis) pallide viridibus striatis convexis nec carinatis; achaeniis nigrescentibus 2.2 mm. longis 0.6 mm. diametro ubique villosis apice rotundatis plus minusve margine squamacea cupulata coronatis. — Iguala Cañon, Guerrero, Mexico, alt. 760 m., 22 September, 1905, C. G. Pringle, no. 10,068 (type, in hb. Gray).

This plant appears to stand near *Eleutheranthera*, with which it shares many characters. It differs, however, markedly in its anthers, which are appendiculate and connate, in its non-accrescent involucre, and densely puberulent achenes. Furthermore in *Eleutheranthera* the achenes have a nipple-shaped contracted summit which is here lacking.

Perymenium globosum Robinson, n. sp., caule quadrangulato grisco-brunneo angulis rotundatis faciebus sulcatis, internodiis 7-9 cm. longis; foliis oppositis petiolatis ovato-oblongis serratis rugosis acuminatis basi rotundatis vel abrupte breveque cuneatis supra scabris strigillosis subtus vix pallidioribus scabriusculis in nervis venisque hispidulo-pubescentibus 8-12 cm. longis 4-5 cm. latis, petiolo 1.8 cm. longo flexuoso supra canaliculato; capitulis corymbosis, corymbis compositis 8-18 cm. latis; bracteis inferioribus foliaceis, bracteolis linearisubulatis 3-5 mm. longis, pedicellis filiformibus flexuosis 1-2 cm. longis adpresse griseo-pubescentibus; involucri squamis ovatis acutis viridibus ca. 3 mm. longis; disco valde convexo; flosculis liguliferis ca. 7, ligulis linearibus aureis patentibus 6-8 mm. longis; paleis oblongis conduplicatis apice vix acutiusculis flavidis; capitulis fructiferis depresso-globosis 8 mm. diametro; achaeniis disci obovatis crassiusculis atrobrunneis plus minusve bullatis 2 mm. longis 1 mm. latis glabris a basi styli conica indurata coronatis; pappi aristis ca. 15 flavidulis inaequalibus plerisque 1 mm. longis. — Uruapan, Michoacan, Mexico. C. G. Pringle, no. 10,354. This species is nearly related to P. verbesinoides DC., but differs in having broader and less attenuate pales, greener involucral scales, and leaves 3-nerved not from the base but from a point nearly 1 cm. above the base.

Verbesina montanoifolia Rob. & Greenm., var. leptopoda Robinson, n. var., pedicellis subaequalibus quam eis formae typicae longioribus (ca. 1 cm. longis) et gracilioribus; capitulis paulo minoribus. — By

streams, Tarascon, Mexico, 28 October, 1905, C. G. Pringle, no. 10,118 (type, in hb. Gray). According to note of Mr. Pringle this variety grows to a height of 3–4.5 m.

Verbesina pedunculosa Robinson, n. comb. Actinomeris pedunculosa DC. Prod. v. 576 (1836). Verbesina Capitaneja Nees, Linnaea, xix. 729 (1847); Rob. & Greenm. Proc. Am. Acad. xxxiv. 540 (1899).

Verbesina pleistocephala Robinson, n. comb. Encelia pleistocephala J. D. Smith, Bot. Gaz. xiii. 189 (1888), & Enum. Pl. Guat. i. 22 (1889). Verbesina Donuell-Smithii Coult. Bot. Gaz. xx. 50 (1895); J. D. Smith, Enum. Pl. Guat. iv. 88 (1895); Rob. & Greenm. Proc. Am. Acad. xxxiv. 556 (1899).

Coreopsis Pringlei Robinson, n. sp., fruticosa ramosa; ramis teretibus a cortice ochraceo-griseo obtectis; ramulis striatis viridibus plus minusve 6-angulatis foliosis; foliis oppositis petiolatis bipinnatifidis pallide viridibus glaberrimis vel vix pilosiusculis 2-4 cm. longis 1-3 cm. latis, segmentis patentibus angustissime linearibus leviter acutatis integris vel cum lobis secundariis paucis similibus instructis 4-16 mm. longis 0.6-0.8 mm. latis; capitibus terminalibus solitariis vel ad 3-5 corymbosis pedunculatis erectis vel nutantibus 3 cm. latis (ligulis patentibus inclusis); pedunculis 1-4 cm. longis nudis vel in media parte cum bractea unica lineari instructis; involucri campanulati squamis exterioribus ca. 8 herbaceis lineari-oblongis 3-5 mm. longis 1 mm. latis apice rotundatis basi pilosiusculis, squamis interioribus ovatooblongis subscariosis acutatis ca. 6 mm. longis striatis flavido-brunneis: ligulis ca. 8 juventate supra aureis subtus flavidis maturitate laete flavis oblongis ca. 1.2 cm. longis 4-6 mm. latis, nervis atrobrunneis: paleis linearibus pallidis brunneo-lineolatis apice obtusis eroso-ciliatis; achaeniis disci linearibus valde obcompressis in facie interiore et in marginibus valde villosis in facie exteriore subglabris 5 mm. longis (vix maturis); pappi aristis 2 pallidis villoso-plumosis attenuatis 3-4 mm. longis. — Dry ledges, San Juan del Rio, Queretaro, Mexico, alt. 1920 m., 8 September, 1905, C. G. Pringle, no. 10,050 (type, in hb. This species is related to C. rhyacophila Greenman, but differs in its linear-oblong round-tipped outer involucral scales and much narrower leaf-segments, as well as in its shorter petioles and more decidedly ligneous stem.

Tridax platyphylla Robinson, n. sp., herba perennis laxe ramosa pubescens; caulibus teretibus viridibus vel purpurascentibus striatulis pubescentibus; foliis membranaceis oppositis petiolatis supra basin 3-nerviis, lamina late ovata 6.3–11.5 cm. longa 4.5–10 cm. lata dentata vel leviter 3-lobata supra viridi sparse pubescenti cum pilis basi tuberculoincrassatis subtus vix pallidiore in nervis appresso-pubescenti apice

acuta vel obtusiuscula vel brevissime acuminata basi cuneato-attenuata; capitibus laxe corymbosis longe pedicellatis radiatis, disco leviter convexo; involucri squamis paucis subaequalibus ovatis vel late oblongis acutis herbaceis hirsutulis ca. 7 mm. longis; flosculis disci numerosis, corollis anguste tubulosis aurantiacis 7 mm. longis externe glabris, tubo proprio brevi basi ampliato; faucibus multo longioribus paulo et gradatim amplioribus 5-nerviis, limbi dentibus 5 brevibus ovato-lanceolatis acutiusculis apice puberulis; achaeniis turbinato-cylindricis 2.8 mm. longis sericeis, pappi setis plumosis numerosis attenuatis plus minusve inaequalibus ca. 2.6 mm. longis; flosculis radiatis 5, ligulis albis late oblongis vel suborbicularibus patentibus apice 3-dentatis 6-10 mm. longis. — River ledges, Balsas Station, alt. 600 m., 27 September, 1905, Guerrero, Mexico, C. G. Pringle, no. 10,075 (type, in hb. Gray). This species is habitally similar to T. tenuifolia Rose, which, however, has smaller leaves and pappus decidedly longer than the achenes.

Galinsoga filiformis Hemsl., var. epapposa Robinson, n. var., habitu foliis inflorescentia, etc., formae typicae simillima; achaeniis omnino epapposis apice annulo albido inconspicuo coronatis; foliis caulinis quam eis formae typicae paululo minoribus. — San Ramón, Durango, Mexico, 21 April-18 May, 1906, Dr. E. Palmer, no. 127 (type, in hb. Gray). This puzzling plant, which according to the notes of the collector was found in numbers, much dried, on stony ridges among trees and bushes, differs in its lack of pappus from any other Galinsoga. Its otherwise close correspondence with G. filiformis, however, would seem to show that it is merely a new instance of a calvous form of an ordinarily pappus-bearing species. Similar cases are familiar in several neighboring genera, e. g. Calea, Jaegeria, etc. The phenomenon seems to present an ecological problem of interest, and it is to be hoped that collectors who have an opportunity to study these plants in the field may bear the matter in mind and endeavor to learn the conditions which determine the presence and absence of pappus in these in other respects essentially identical forms.

Flaveria bidentis Robinson, n. comb. Ethulia bidentis L. Mant. i. 110 (1767). Flaveria chilensis Gmel. Syst. 1269 (1796); Johnston, Proc. Am. Acad. xxxix. 285 (1903). Milleria Contrayerba Cav. Ic. Pl. i. 2, t. 4 (1791). The author has examined the type of Ethulia bidentis in the Linnaean Herbarium and finds that, as given in the Index Kewensis, it is the plant which has long passed as Flaveria Contrayerba. The Vienna rules of nomenclature require the restoration of the earlier specific name.

Pericome macrocephala Robinson, n. sp., griseo-pulverula vel

puberula oppositiramea; caulibus fragilibus subteretibus leviter angulato-striatis glabriusculis brunneis paulo lignescentibus; foliis triangulari-hastatis 5-6 cm. longis 4-5 cm. latis caudato-attenuatis subintegris basi abrupte cuneatis, auriculis subacuminatis, petiolo gracili 2-2.7 cm. longo; inflorescentiis corymbosis terminalibus 6-8 cm. latis subplanis 9-15-capitulatis; pedicellis gracilibus rectis vel leviter arcuatis sursum modice incrassatis pubescentibus 1-2 cm. longis; capitulis 1.7 cm. longis 1.2 cm. diametro homogamis multiflosculosis; involucri cupula ovoideo-subcylindrata 1.2-1.4 cm. longa griseo-puberula multistriata dentibus brevissimis caudiformibus plus minusve patentibus; corollis laete flavis 1 cm. longis, tubo proprio gracillimo 3 mm. longo glanduloso-puberulo, fancibus anguste tubulosis sursum paululum ampliatis, dentibus limbi 4 brevibus ovato-oblongis obtusis; achaeniis nigrescentibus anguste oblongis valde compressis margine et apice fimbriatociliatis. — A showy plant growing in large masses on talus in mountains near San Ramón, Durango, Mexico, 21 April-18 May, 1906, Dr. E. Palmer, no. 69 (type, in hb. Gray). In habit and floral structure this species closely approaches P. caudata Gray, but differs from it conspicuously in having heads nearly twice as large. The form of the involucre also is different, being ovoid-subcylindric in the species here described while it is considerably more campanulate in P. caudata.

Loxothysanus Robinson, n. gen, Compositarum Heleniearum. Capitula homogama. Involucrum campanulatum vel turbinatum. squamis paucis uniseriatis aequalibus plerumque obovatis vel oblanceolatis acutis vel saepissime obtusiusculis herbaceis puberulis. Receptaculum parvum planiusculum onustum. Flosculi modice numerosi tubulosi hermaphroditi fertiles. Corollae albidae, tubo proprio gracili puberulo vel glandulifero fauces campanulatas subaequante, limbo 5-Styli rami breves recurvati filiformes vix infra apicem incrassati brevissime et obtusiuscule appendiculati. Antherae basi breviter sagittato-auriculatae apice obtuse appendiculatae. Achaenia gracilia 5angulata sursum hispidula deorsum longiuscule angustata. Pappi squamae 5-8 oblongae erosae eis in margine exteriore achaenii quam aliis valde brevioribus. — Frutices humiles vel suffrutices ramosi erecti vel procumbentes. Capitula pauca mediocra axillaria vel laxe corymbosa. Flosculi vel omnes regulariter 5-dentati vel exteriores obscure subbilabiati. Folia opposita petiolata, limbo ovato vel orbiculari paucilobato vel vix crenato. (Nomen a λοξός, obliquus, et θύσανος, fimbriae, pappum unilateraliter abbreviatum designat.)

L. sinuatus (Less.) Robinson, n. comb., foliis ovatis sinuatis plerumque 3-lobatis basi obtusis vel subtruncatis vel late cordatis; capitulis

corymbosis; involucri squamis ca. 12 oblanceolatis acutis vel acutius-culis. — Bahia sinuata Less. Linnaea, v. 160 (1830). B. nepetaefolia Gray, Proc. Am. Acad. v. 184 (1861). — On rocky soil in Central and Southern Mexico. The following specimens have been examined. On cliffs near Hacienda de la Laguna, Schiede, no. 358 (hb. Berlin, fragments in hb. Gray); between San Luis Potosi and Tampico, Palmer, no. 1090 (hb. Gray); bare mountain ledges, Tamasopo Cañon, San Luis Potosi, Pringle, no. 3096 (hb. Gray); Wartenburg near Tantoyuca, prov. Huasteca, Ervenberg, no. 65 (hb. Gray); steep banks of barrancas, Zacuapan, Vera Cruz, Purpus, no. 1862, in part (hb. Gray).

L. filipes Robinson, n. sp., fruticulus gracillimus procumbens ramosus; ramis curvato-ascendentibus foliatis breviter pubescentibus; foliis graciliter petiolatis, limbo suborbiculari 1-1.8 cm. diametro crenato supra viridi obscure tomentello subtus incano-tomentello; petiolo 1-1.5 cm. longo filiformi flexuoso puberulo; capitulis ca. 30-floris axillaribus; pedunculo 2-3.5 cm. longo filiformi; involucri subturbinato-campanulati squamis ca. 7 obovatis obtusiusculis anthesi ca. 3 mm. longis; corollis 2.8 mm. longis, tubo proprio gracili glanduloso-puberulo ca. 1 mm. longo, faucibus campanulatis limbum fere aequantibus; pappi squamis interioribus ca. 0.4 mm. longis exterioribus 0.2-0.3 mm. longis; achaeniis 2.8 mm. longis deorsum valde angustatis. — Steep banks of barrancas, Zacuapan, Vera Cruz, Mexico, May, 1906, Purpus, no. 1862, in part (type, in hb. Gray).

This plant, which was sent to the writer by Mr. T. S. Brandegee, proves to be a near relative and evident congener of the problematic species originally decribed as *Bahia sinuata* by Lessing and later redescribed by Dr. Gray as *B. nepetaejolia*. Both plants differ from the more typical species of *Bahia* in general habit, in the broad leaf-blades, which are very shallowly if at all cleft or lobed, in the absence of rays, and in the strongly unsymmetrical pappus. To judge from Dr. Gray's description and notes relating to his *B. nepetaefolia*, he was much inclined to regard the plant as belonging to a separate genus and only referred it to *Bahia* from a reluctance to increase the number of monotypic genera. The discovery by Mr. Purpus of a second plant maintaining perfectly the generic distinctions of the first seems now to warrant fully the recognition of the two as an independent genus.

Tagetes stenophylla Robinson, n. sp., perennis erecta usque ad 1 m. altitudine ramosa glaberrima basi suffrutescens; canle tereti costato folioso glaucescenti; ramis ascendentibus gracilibus in pedunculos longos nudos apicem versus purpurascentes et modice incrassatos terminantibus; foliis 2-4 cm. longis pinnatifidis, rhachi anguste lineari, segmentis etiam linearibus angustissimis utrinque ca. 3 acutis vel setu-

liferis simplicibus vel semel lobatis, lobis similibus angustis; pedunculis 5–10 cm. longis apice saepe nutantibus; involucri anguste ovoidei 1.5 cm. longi basi rotundati vel paulo turbinati pallidi vel purpureotineti squamis 5 alte connatis a lineis binis glandularum linearum notatis apice aureis obtusis tomentosis; flosculis liguliferis 5; ligulis aureis obovato-oblongis 10–12 mm. longis 6–8 mm. latis apice obcordatis saepe obliquis; achaeniis disci compressis lineari-oblongis nigrescentibus 3 mm. longis sursum strigillosis; pappi aristis 5 connatis quarum 2 multo longioribus apice liberis attenuatis sursum barbellatis. — Dry soil of fields near Uruapan, Michoacan, Mexico, 25 January, 1907, C. G. Pringle, no. 10,361 (type, in hb. Gray). This species has much in common with P. linifolia Seaton, but differs from it in having more deeply colored rays and obtusish not at all caudate-acuminate teeth of the involucral cup.

Cacalia Goldsmithii Robinson, n. sp., perennis herbacea erecta, caudice parvo ovoideo sursum fulvo-lanato; caule subrecto vel leviter flexuoso glabro simplici gracili 1-2-foliato 6-7 dm. alto; foliis radicalibus longe petiolatis ovatis repando-dentatis vix lobatis 1 dm. longis 6-9 cm. latis pinnatim nervatis firmiusculis utrinque glabris laxe reticulatis apice rotundatis basi late cordatis, dentibus cuspidatis, nervis venisque utrinque prominulis, petiolo gracili nudo 14-16 cm. longo basi vix dilatato: folio caulino inferiore radicalibus simili sed minore basi obtuso nec cordato petiolo 12 cm. longo flexuoso nec appendiculato nec auriculato; folio caulino superiore multo minore oblongo dentato, petiolo 2 cm. longo basin versus modice ampliato caulem amplectente : corymbis compositis planis ca. 50-capitulatis; bracteis linearibus; capitulis ca. 13-floris contiguis; involucri simplicis haud calveulati campanulatosubcylindrici squamis ca. 8 oblongis 7 mm. longis 2-3 mm. latis dorso planiusculis apice obtusiusculis ciliatis; corollis albido-ochroleucis 8 mm. longis fere ad mediam partem quinquifidis, lobis oblongis obtusis; pappi setis sordidis tubum proprium vix superantibus; achaeniis compressis breviter oblongis glabris. — On level pastures, Hacienda San Marcos, Jalisco, Mexico, alt. about 350 m., 12 July, 1905, Rev. P. Goldsmith, no. 8 (type, in hb. Gray). This species is probably nearest C. Palmeri Gray, but differs in its thinner smooth ovate rather than suborbicular leaves as well as in its larger more numerously flowered heads.

Cacalia Holwayana Robinson, n. sp., herbacea erecta 1-2 m. alta; caule tereti medulloso striato atropurpureo glanduloso-puberulo; radicibus carnosis; foliis longipetiolatis orbicularibus subcentrali-peltatis 9-13-sinuato-lobatis supra laete viridibus subtus vix pallidioribus utrinque sparse pubescentibus laxe reticulato-venosis 1.5-2 dm. diametro, lobis acutis 2-4 cm. longis 1.5-5 cm. latis oblongis sinuato-

dentatis (nec lobatis) et cuspidato-denticulatis; petiolo 1.5-2 dm. longo atropurpureo griseo-piloso; inflorescentia ampla pyramidata, bracteis inferioribus saepe petiolatis foliis similibus sed multo minoribus, bracteis superioribus angustissime linearibus vel subfiliformibus atropurpureis glanduloso-pilosis; capitulis numerosis in summis ramis ramulisque nutantibus ca. 10-floris 2 cm. longis; involucri subcylindrici calyculo bracteolarum subfiliformium suffulti squamis lineari-lanceolatis ca. 10 ca. 1.5 cm. longis in carina atropurpurea griseo-puberulis margine albido subscarioso levibus; corollis 13 mm. longis glabris, tubo proprio gracili 8 mm. longo, faucibus vix ullis, limbo in lobis linearibus profunde partito; achaeniis 5 mm. longis adpresse tomentulosis; pappi setis tenuibus laete albis corollam aequantibus. — Uruapan, Michoacan, Mexico, 11 October, 1899, E. W. D. Holway, no. 3617 (type, in hb. Gray); 12 November, 1905, C. G. Pringle, no. 13,672; in granitic soil on the Sierra Madre of Michoacan or Guerrero, alt. 1100 m., 6 September, 1898, E. Langlassé, no. 576. This species is near C. peltata HBK., but is readily distinguished by its leaves, which are less deeply lobed, the lobes not again sinuately lobed, and by the smaller exceedingly narrow bractlets, those of C. peltata being foliaceous.

Cacalia Laevigata Sch. Bip. ex Klatt, Leopoldina, xxiv. 125 (1888). Senecio heteroideus Klatt, l. c. (1888). Cacalia longipetiolata Robinson & Greenman, Am. Jour. Sci. l. 157 (1895). When in 1895 the authors of C. longipetiolata characterized that species they knew C. laevigata only from Klatt's description. A drawing and some fragments of the type of C. laevigata, subsequently received at the Gray Herbarium by the purchase of the Klatt Herbarium, prove beyond doubt the identity of C. longipetiolata with C. laevigata, a correspondence which could scarcely have been inferred from the brief and in some respects misleading characterization of C. laevigata given by Klatt.

Cacalia michoacana Robinson, n. sp., herbacea perennis pilis crispis griseis puberula ca. 9 dm. alta; caule simplici leviter flexuoso striato atropurpureo medio folioso basi et apice nudiusculo; caudice crasso lanato; foliis ca. 10 suborbicularibus palmato-lobatis 3–6 cm. longis 5–8 cm. latis crassiusculis utrinque reticulato-venulosis et in venis puberulis supra laete viridibus subtus pallidioribus basi subtruncatis vel latissime cordatis, lobis 5–7 brevibus triangularibus margine cuspidato-denticulatis; capitulis ca. 6 ramos ascendentes inflorescentiae terminantibus ca. 30-floris 1.5 cm. longis 2 cm. diametro longe pedicellatis; involucri atropurpurei campanulato-subcylindrici squamis principalibus ca. 15 lineari-lanceolatis dorso atropurpureis carinatis margine albis tenuibus subscariosis, involucro basi squamis minimis calyculato; corollis 1 cm. longis, tubo proprio viridescenti gracillimo 5 mm. longo,

faucibus cylindricis et limbo 5-lobato flavescentibus, lobis linearibus recurvatis; pappi setis laete albis tenuibus aequalibus corollam fere aequantibus. — On pine-covered crater cone, Uruapan, Michoacan, Mexico, alt. 1680 m., 31 October, 1905, C. G. Pringle, no. 10,117 (type, in hb. Gray). Habitally near C. laevigata Sch. Bip., but differing conspicuously in its considerably smaller heads, narrower carinate dark purple involucral bracts, and less deeply lobed leaves.

Perezia arachnolepis Robinson, n. sp., herbacea erecta a basi plus minusve decumbenti 1.5 m. alta; caule tereti striato purpureo glabro usque ad inflorescentiam perlaxam simplici; caudice fulvo-lanato; radicibus fibriformibus duris atrobrunneis; foliis oblanceolato-oblongis vel ohlongo-linearibus sessilibus sagittato-amplexicaulibus usque ad 1.6 dm. longis 1.7-5.8 cm. latis firmis utrinque viridibus reticulatis supra glabris subtus vix pallidioribus sparse puberulis vel glabris argute denticulatis apice acutis vel breviter acuminatis; inflorescentia perlaxa 8-16-capitata; capitibus ramos elongatos sursum valde squamosos terminantibus ca. 3 cm. diametro; involucro valde turbinato, bracteis pedunculi in squamas involucri gradatim transeuntibus anguste lanceolatis vel linearibus apice subulatis margine arachnoideo-lanatis; corollis purpureis 1.3 cm. longis glabris; antheris etiam purpureis; achaeniis atrobrunneis sursum hispidulis 3 mm. longis. — Cañons, Chapala Mountains near Guadalajara, Jalisco, Mexico, 13 December, 1889, C. G. Pringle, no. 2935 (type, in hb. Gray), and in barranca of Rio Blanco near Guadalajara, 29 November, 1905, C. G. Pringle, no. 13.668 (hb. Gray).

Perezia lepidopoda Robinson, n. sp., precedenti valde affinis herbacea erecta 7-8 dm. vel ultra alta glaberrima; caule purpureo recto tereti striato foliosissimo in parte superiore ramos simplices valde patentes multi-bracteatos unicapitatos gerente; foliis anguste oblongis vel oblongo-linearibus attenuatis acutissimis saepissime recurvatis vel reflexis conduplicatis subcartilagineis concoloribus sessilibus sagittatovel hastato-amplexicaulibus argute et dupliciter sinuato-dentatis 6-13 cm. longis 8-22 mm. latis utrinque glabris viridibus reticulato-venosis. dentibus lanceolato-subulatis 2-4 mm. longis divaricatis acutissimis; ramis pedunculiformibus ca. 12 cm. longis a bracteis numerosissimis fere a basi sed praesertim apicem versus tectis, bracteis inferioribus 1-2 cm. longis anguste lanceolatis sagittatis denticulatis, superioribus anguste linearibus peracutis adpressis hinc inde contortis in squamas involucri gradatim transeuntibus; capitibus (omnibus valde immaturis) usque ad 3 cm. diametro multifloris; involucri turbinati squamis lineari-lanceolatis acutissimis viridibus vel purpurascentibus striatulis obsolete puberulis. — Valley near Cuernavaca, Morelos, Mexico, alt.

1220 m., 17 October, 1900, C. G. Pringle, no. 9253 (type, in hb. Gray). This species is clearly separated from the preceding by its much narrower leaves and merely puberulent more subulate involucral scales. It belongs to a group of several obviously diverse yet nearly related plants which have been provisionally referred to the merely inferential P. turbinata La Llav. & Lex. The latter, however, described as having ovate leaves and short-peduncled heads, must certainly have been a plant quite different from either here characterized.

## III. NEW PLANTS FROM GUATEMALA AND MEXICO, COLLECTED CHIEFLY BY C. C. DEAM.

BY B. L. ROBINSON AND H. II. BARTLETT.

Polypodium (Goniophlebium) hispidulum Bartlett, n. sp., rhizomate crassitudine 3-5 mm. simplici vel furcato ad arborum truncos repenti longitudine usque ad 12 cm., aetate aperto foveolato-rugoso juventate paleis tecto, paleis deltoideo-linearibus secus lineam medianam ferrugineis margine straminellis; frondibus inter se propinquis 6-12 cm. longis 4-7.5 cm. latis; stipitibus gracilibus 0.5-3.5 cm. longis exigue pilosis supra canaliculatis subtus semiteretibus; laminis fere usque ad costam pinnatipartitis utrinque hispidulis atroviridibus circumscriptione valde variabilibus ovatis semiovatis vel aequilateraliter triangulis prout segmenta duo inferiora reducta aut haud reducta sunt: segmentis integerrimis approximatis lanceolatis 3-9-jugis basi dilatatis confluentibus apice obtusis, maximis 6 mm. latis 3.5 cm. longis, terminale 1.5-6 cm. longo maxime variabili; nervo mediano flexuoso. nervis lateralibus alternis utrinque 10-11 haud procul a basi furcatis, ramis anticis liberis in segmentis superioribus soriferis, ramis posticis arcuatis marginem nec attingentibus, aut simplicibus aut furcatis aut anastomosantibus areolarum seriem unam formantibus; soris rotundis medio inter nervum medianum et marginem uniserialiter dispositis ca. 1 mm. diametro; sporangiis glabris ca. 20. — Los Amates, Department of Izabal, Guatemala, 11 February, 1905, C. C. Deam, no. 117 (type, in hb. Gray). The same fern, collected by Tuerckheim at Cubilquitz, Department of Alta Verapaz, December, 1900, was distributed as Polypodium pubescens Hook, et Grev., in John Donnell Smith's "Plants of Guatemala," no. 8053. P. pubescens is, without doubt, the nearest related species to P. hispidulum. It has, however, a much larger frond, with irregularly laciniate segments, which at the base of the frond are

widely separated and not at all confluent. The segments are also prevailingly opposite in *P. pubescens*, whereas in *P. hispidulum* they are alternate.

Paspalum guatemalense Bartlett, n. sp., perenne 6 dm. altum simplex vel ramosum; internodiis glabris lateraliter compressis, acie ad folii axillam versus canaliculatis; foliorum vaginis equitativis pilosis (praecipue juxta margines et ad ligulae basin) quam internodiis aut brevioribus aut longioribus margine brunneo-scareosis; ligula 2.5 mm. longa textura marginibus vaginarum simili; laminis lineari-lanceolatis 10-15 mm. latis 6-15 cm. longis apice acutis basi rotundatis vel subcordatis utrinque dense pilosis; spicis 1-3 sessilibus inter se 2.5-3.5 cm. distantibus 3-6 cm. longis; rhachi angusta glabra vel scabriuscula; pedicellis minute hispidulis; spiculis geminatis altera breviter altera longius pedicellata, geminis secus rhachin in seriebus duabus alternis; spiculis suborbicularibus 2.1 mm. longis 1.9 mm. latis glabris albicantius viridibus antice planis postice valde convexis; gluma inferiore in spiculis geminorum superioribus suborbiculari apice rotundata quam spicula 6-plo breviore, in spiculis geminorum inferioribus longiore eccentrica late ovata obtusa vel acutiuscula; gluma secunda membranacea quam spicula paulo breviore 5-nervata, nervis juxta marginem anastomosantibus ad apicem in mucronem perbrevem terminantibus; gluma tertia membranacea quam secunda longiore 3 (-5)-nervata; gluma quarta paleaque cartilagineis obscure nervatis; staminibus stylisque ut in speciebus generis reliquis. — A swamp at Gualan, Department of Zacapa, Guatemala, January 20, 1905, C. C. Deam, no. 427 (type, in hb. Gray). P. quatemalense is a member of Fournier's genus Dimorphostachus. Following his arrangement of the group, the affinity of the new species is with Dimorphostachys Schaffneri Fourn., D. variabilis Fourn., and D. Ghiesbreghtii Fourn. Of these, only D. Schaffueri is represented in the Gray Herbarium. It may be at once distinguished from P. quatemaleuse by its glabrous foliage and larger ovate spikelets, acute at the apex. D. variabilis and D. Ghiesbreahtii both have pubescent spikelets, whereas those of P. quatemalense are perfectly glabrous.

Streptochaeta Sodiroana Hack. Noteworthy among the plants collected by Mr. C. C. Deam in Guatemala is a specimen of the anomalous South American genus Streptochaeta. The genus consists of two species, and in its spirally arranged (not distichous) flower-scales forms a unique exception among the genera of grasses. When the generic affinity of Mr. Deam's plant was discovered, it became evident that the species might be identical with the Ecuadorian S. Sodiroana Hack. A portion of the specimen was sent to Professor Hackel, who has kindly

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confirmed the apparent identity. This is by no means an isolated case of the occurrence of identical species in Ecuador and Guatemala, but it has peculiar interest from the marked character and rarity of the plant concerned. Mr. Deam's specimens were collected at Los Amates, Guatemala, 10 February, 1905, and distributed as no. 97 of his set. He writes that only a few plants were found, and that these were growing in rather wet situations deep in the virgin forest. An interesting morphological as well as systematic account of the species is given in Professor Hackel's original characterization, Oest. Bot. Zeitschr. xl, 111 (1890).

Fuirona zacapana Bartlett, n. sp., rhizomate perpendiculari elongato modice incrassato; culmis 9 dm. longis gracilibus ascendentibus hispidis vel ad basin glabriusculis ca. 8-foliis; foliorum vaginis 1.5-3 cm. longis dense hispidis; foliis linearibus utrinque hispidis usque ad 5 mm. latis, in partibus culmi inferioribus 1 cm. longis superne 9 cm. longis; capitulis 3-4, infimo solitario in axilla folii supremi pedunculato, reliquis plus minusve approximatis; spiculis in capitulo quoque 3-6 ovatis 4 mm. latis 8 mm. longis; squamis brunneis pubescentibus in spiculae basi suborbiculatis in apice ovatis trinerviis, in dorso rectiaristatis; sepalis 3 brunneis glabris duriusculis ovatis basi subcordatis longe unguiculatis apice rotundatis infra apicem in dorso breviaristatis. aristis retrorsum scabris; setulis 3 cum sepalis alternantibus superne retrorsum scabris quam achaenio multo brevioribus; achaenio longe stipitato mucronato sepala paene aequante. — In swamps, Gualan, Department of Zacapa, Guatemala, 13 January, 1905, C. C. Deam, no. 423 (type, in hb. Gray). This very distinct species is nearest to F. simplex Vahl, from which it differs in its lax habit, in the extreme development of pubescence on the leaf-sheaths, in its short perianthbristles, and long-stiped achene.

Myriocarpa malacophylla Robinson & Bartlett, n. sp., arborea 4 m. altitudine; ramis curvatis crassiusculis molliter lignosis siccitate corrugato-rugulosis pallide griscis juventate tomentosis actate glabratis, lenticellis paucis sparsis; foliis membranaceis late ovatis cordatis breviter caudato-acuminatis serratis 17 cm. longis 11 cm. latis supra more generis sparse pilosis et cystolithis radiantibus instructis subtus molliter tomentosis griscis, apice caudiformi ca. 1 cm. longo, nervis lateralibus utrinque 4-5; petiolo 1.7-2 cm. vel ultra longo tomentoso; inflorescentiis omnino sessilibus ca. 1 cm. supra basin furcatis; ramis 1-2 dm. longis grisco-tomentosis unilateraliter floriferis; floribus ♀ arcte sessilibus; calyculo 2-phyllo brevissimo villoso; ovario lenticulari-ovoideo 0.7-0.9 mm. longo villoso-hispidulo; floribus ♂ etiam sessilibus, sepalis 4 ovatis obtusis villosis, staminibus 4. — Gualan,

Department of Zacapa, Guatemala, 12 January, 1905, C. C. Deam, no. 361 (type, in hb. Gray); Maria Madre Island, Tres Marias Islands, May, 1897, E. W. Nelson, no. 4275 (hb. Gray). This species appears to be either monoecious, as in Mr. Deam's specimen, which has staminate flowers at the base of some of the pistillate inflorescences, or it may be dioecious, as in Mr. Nelson's specimen, in which all the flowers are staminate. The species appears to stand nearest M. cordifolia Liebm., but differs in its ovate rather than suborbicular less rugose leaves and wholly sessile inflorescences.

Polygonum longiocreatum Bartlett, n. sp., caule simplici ca. 7 dm. alto, ad nodos inferiores radicanti; internodiis 1.5-2 cm. longis glabris; ocreis cylindricis eciliatis 1.5-1.7 cm. longis, in parte inferiore caulis quam internodiis brevioribus, plus minusve inflatis, in parte superiore imbricatis; foliis lanceolatis 1.5-3 cm. latis 9-13 cm. longis perbreviter petiolatis, apice basique acutis, utrinque glabris pellucidopunctatis, margine nervisque subtus scabris; spicis ca. 9, paniculatis erectis 4-5 cm. longis; pedunculis pedicellisque glabris; ocreolis rubris 2 mm. longis tri-vel quadrifloris; calyce rubro 5-partito; staminibus 7 styloque (solum in extremo bifido) inclusis; achenio lenticulari 2 mm. longo nigro, ad basin rotundato, ad apicem abrupte acuto, faciebus convexis. — In a swamp at Gualan, Department of Zacapa, Guatemala, January 14, 1905, C. C. Deam, no. 374 (type, in hb. Gray). The obvious affinity of P. longiocreatum is with Polygonum spectabile Mart., from which it differs in not having glandulose-scabrous peduncles. his treatment of P. spectabile in De Candolle's Prodromus, Meisner cites two earlier-published species of Weddell as possible synonyms. Dr. Small accepts, in his "Monograph of the N. A. Species of Polygonum," one of Weddell's names, Polygonum ferrugineum, as an available name for P. spectabile Mart. Whether he applies the name correctly or not, P. longiocreatum may be distinguished from the P. ferrugineum of Small's monograph by the style, which in the former is bifid only at the end, and by the long pedicellate flowers, small achenes, and short-petioled leaves.

Ruprechtia Deamii Robinson, n. sp., fruticosa (9 solum visa); ramis flexuosis glabris in specimine exsiccato sulcato-rugosis brunneis, internodiis 7-30 mm. longis, ocreis membranaceis griseo-castaneis vix 0.6 mm. longis; foliis magnis oblongis coriaceis penninerviis 10-18 cm. longis 5.5-8 cm. latis integerrimis concoloribus utrinque prominulenter reticulato-venulosis subtus in nervis patenter fulvo-pubescentibus et in venulis puberulis, basi rotundatis vel modice angustatis, apice obtusis vel rotundatis, petiolo brevissimo crassiusculo supra leviter canaliculato ca. 3 mm. longo; racemis numerosis fructiferis 2-6 cm. longis solitariis

vel usque ad 3 fasciculatim aggregatis patentibus vel deflexis subdensifloris, tomentosis; bracteis ovatis subacuminatis brunneis adpresse villosis: pedicello fructifero filiformi 2-3 mm. longo tomentoso; calvee fructifero ca. 3.5 cm. longo, tubo anguste ovoideo molliter subadpresse tomentoso ca. 6-7 mm. longo ca. 4 mm. diametro, alis 2.5 cm. longis 5 mm. latis spatulato-oblongis glabriusculis 3-nerviis reticulato-venosis apice rotundatis pallide viridibus subdiaphanis; sepalis interioribus subulatis glabris, parte libera ca. 4 mm. parte adnata ca. 1.5 mm. longa; achaenio attenuato-ovoideo obtusissime trigono, angulis tumidis leviter sulcatis in parte superiore sulci pubescentibus; stylis liberis, stigmatibus linearibus recurvatis. — Gualan, Department of Zacapa, Guatemala, alt. 128 m., January 11, 1905, C. C. Deam, no. 231 (type, in hb. Gray). This species belongs to the § Hexasepalue of Meisner, and § Pseudoruprechtia of Bentham and Hooker, these authors dividing the genus on different characters. It is nearly related to R. Cumingii Meisn., known to the author only from Meisner's description (DC. Prod. xiv, 179). If the characters there given are correct, the plant here characterized is certainly distinct, as is shown by its larger leaves, longer calvx, the presence of pubescence on the lower surface of the leaves, decidedly rugose branches, spreading or deflexed racemes, etc.

Aeschynomene Deamii Robinson & Bartlett, n. sp., fruticosa 2 m. alta laxe ramosa aspectu glabra; caulibus teretibus lignescentibus striatulis fusco-brunneis glabris; foliis petiolatis oblongis 5-7 cm. longis; foliolis ca. 18-jugis lineari-oblongis glabris utrinque viridibus supra minutissime nigro-punctatis subtus pinnatim venosis basi obliquis apice rotundatis mucronatis 9-10 mm. longis 2 mm. latis; rhachi supra sparse puberula subtus glabra; petiolo 1 cm. longo; stipulis 1.5 mm. longis subulatis brunneis acutissimis; racemis axillaribus 2-7-floris; pedunculis 10-17 mm. longis filiformibus glabris; bracteis ovatis herbaceis margine scariosis apice acutis supra basin affixis basi rotundatis liberis; pedicellis anthesi ca. 4 mm. longis fructiferis ca. 6 mm. longis; calvee glabro 2-partito, labio dorsali ovato ca. 7 mm. longo ca. 5.5 mm. lato obtusiusculo, labio ventrali angustiore ca. 9 mm. longo acuto; vexillo obovato 12 mm. longo 10 mm. lato apice rotundato basi modice angustato; alis semiobovatis basi a latere superiore obtuse auriculatis; carinae petalis ca. 11 mm. longis; staminibus quinis connatis; legumine ca. 13-seminato ca. 1 dm. longo 6.5 mm. lato fragili utrinque undulato, segmentis subquadratis margine crassiusculo faciebus glaberrimis levibus modice nervosis nec rugosis; seminibus atrobrunneis lunatis levissimis subnitidis 5 mm. longis 3 mm. latis. — San Felipe, Department of Izabal, Guatemala, 15 February, 1905, C. C. Deam, no. 26 (type, in hb. Gray). In its numerous leaflets of oblong-linear shape this species somewhat resembles A. americana L., A. hispida Willd., and A. sensitiva Sw. It has, however, flowers which are much larger than those of A. sensitiva, and somewhat larger than those of the other species mentioned. It differs furthermore from A. hispida in its entire not dentate bracts, and from both A. americana and A. hispida in its essentially glabrous foliage and fruit.

Cassia emarginata L., var. subunijuga Robinson & Bartlett, n. var., foliolis saepissime 2 late oblongo-ellipticis 6-7 cm. longis 4-5 cm. latis supra molliter pubescentibus subtus flavido-tomentosis. — Gualan, Department of Zacapa, Guatemala, 15 January, 1905, C. C. Deam, no. 220 (type, in hb. Gray). This variety appears to agree in flowers and fruit with the typical form, but it is noteworthy in habit by reason of the striking reduction in the number of leaflets to two. Occasionally, however, leaves with four leaflets occur on individuals on which most of the leaves have but two leaflets; so there is reason to suppose that the plant is merely a varietal development from a form with more numerous leaflets, rather than a separate species.

Mimosa (Habbasia) gualanensis Robinson & Bartlett, n. sp., ser. Leptostachyarum, caulibus gracilibus lignosis 4 m. longis aculeatis tomentellis, aculeis sparsis parvis valde recurvatis compressis inaequalibus maximis vix 2 mm. longis brunneis; foliis majusculis 27 cm. latis; pinnis 3-jugis 9-14 cm. longis; foliolis obovato-oblongis 2-4-jugis 4-5 cm. longis 2.4-3 cm. latis firmiusculis supra reticulatis utrinque glabris. petiolo 7 cm. vel ultra longo rhachique valde armatis aculeis sparsis numerosis recurvatis 0.7-2 mm. longis; rhacheolis etiam basin versus aculeolatis; spicis gracilibus 5 cm. longis densifloris breviter pedunculatis, pedunculis tomentellis; floribus 2 mm. longis; calvee 1.2 mm. longo campanulato brevissime 5-dentato extus tomentello; petalis 5 calyce subduplo longioribus oblanceolato-oblongis; staminibus 10 maturitate modice exsertis; legumine immaturo 10 cm. longo 1.3 cm. lato 15-seminato plano tenui glabriusculo leviter arcuato, stipite crassiusculo tomentello tereti 5-6 mm. longo. — Gualan, Department of Zacapa, Guatemala, 19 January, 1905, C. C. Deam, no. 224 (type, in hb. Gray). This species, although clearly of the Leptostachyae, does not appear to be very closely related to any other. It should probably be placed near M. guatemalensis Benth., and M. spirocarpa Rose.

Tetrapteris emarginata Bartlett, n. sp., fruticosa procumbens 3-5 m. longa; ramis oppositis glabris griseo-brunneis; ramulis viridibus nigro-punctatis; foliis oppositis, aetate utrinque glabris, juventate albo-sericeis pilis mox deciduis, forma valde variabilibus, in ramulo florifero sessilibus vel perbreviter petiolatis suborbiculatis 1-1.5 cm. diametro cordatis emarginatis saepe mucronulatis, in ramulo foliifero

breviter petiolatis ovatis 4 cm. longis basi obtusis apice acutis; ramulis floriferis in quasi-umbellas quadrifloras terminantibus; pedunculis 7-8 mm. longis cum pedicellis aequilongis articulatis; bracteis pedunculorum bracteolisque pedicellorum lanceolatis minutis; sepalis 5 albicantius viridibus 2 mm. longis, 4 basi biglandulosis glandulis magnis; staminibus glabris calycem valde superantibus, omnibus basi coalitis; ovariis in unum pyramidatum faciebus concavis coalitis; fructu albolanuginoso dorso medio cristato crista integra glabra; fructus alis glabris viridibus rubro-tinctis anguste oblongis, duobus exterioribus ca. 13 mm. longis, duobus interioribus ca. 9 mm. longis. Petala non visa. — Gualan, Department of Zacapa, Guatemala, January 19, 1905, C. C. Deam, no. 150 (type, in hb. Gray). Tetrapteris emarginata belongs among the glabrous-leaved species of Jussieu's § Tetrapteris \* Anisopterae. It may be easily distinguished from any of the Mexican species by the leaves of the flowering branches.

Euphorbia ephedromorpha Bartlett, n. sp., basi lignescenti; ramis prostratis modice crassis longitudine usque ad 10 dm. saepe simplicibus viridibus flexuosis aphyllis juventate valde compressis, aciebus ambabus bialatis; internodiis 2-4 cm. longis minute granulatis glabratis vel perexique pilosis, in marginibus alarum minutissime scabratis: nodis haud incrassatis corpore papillato (nonne cum folio aequivalenti?) praeditis; stipula una glanduliformi crateriformi pilosa recte super papillam (de qua vide supra) et quam eandem parviore; cymis axillaribus et terminalibus dichotomis 2-12-cyathiis valde glanduloso-pilosis bracteatis; bracteis ad dichotomias oppositis 1.8 mm. longis linearispatulatis dense glanduloso-pilosis; cyathiis anguste conicis 3 mm. longis glanduloso-pilosis; pedicellis gracilibus cyathiis aequilongis; involucri segmentis propriis perbrevibus flabelliformibus ad mediam digitatim 7-8-laciniatis; glandulis 5 planis transverse ovatis marginatis appendiculatis; appendicibus rectis quam glandulo 8-plo quam involucri segmentis triplo longioribus anguste spatulatis glabris; stylo brevi usque ad basin bifido; ovario 2 mm. longo glabriusculo stipitato, stipite cyathio paulo longiore; seminibus lilacinis ovoideis foveolatis. — Gualan, Department of Zacapa, Guatemala, 11 January, 1905, C. C. Deam, no. 232 (type, in hb. Gray). In regard to this species Mr. Deam writes: "I recall the place where it grew very vividly. There is a road leading from Gualan to the Motagua River, and as is the case with all travelled ways in Guatemala, it is washed into deep gullies. This plant (no. 232) was found in the nude, rocky, dry soil at the side of the road, on an angle of about 75°. It grew prostrate in patches extending over an area perhaps six feet square. The soil was of a red type, similar to that around Chattanooga and Atlanta. I did not see it in any other

place." Euphorbia ephedromorpha, a unique plant in both habital and technical characters, belongs to the § Alectoroctonum. The only Euphorbia of the same affinity which has been seen is in the Gray Herbarium from Cerro Quiengola, Oaxaca, Mexico, Caec. et Ed. Seler, no. 1611. It represents a clearly distinct new species of very similar habit, but it cannot be described on account of the scantiness of the material.

Acalypha euphrasiostachys Bartlett, n. sp., fruticosa ramosa 1 m. altitudine; ramulis junioribus molliter pubescentibus ochraceis aetate glabriusculis rubentibus; foliorum limbis ovatis 3-8 cm. longis 2-4.5 cm. latis dentatis utrinque molliter pubescentibus vel supra solum secus nervos pilosis, apice acutis vel caudato-acutis, basi maxime variabilibus acutis rotundatis vel subcordatis; petiolis limbo ca. quintuplo brevioribus; spicis masculis axillaribus sessilibus ca. 1 cm. longis nunquam ad basin bracteis femineis praeditis; spicis femineis axillaribus 2.5-7 cm. longis 4-7-bracteatis, dispositione formaque bractearum speciebus alpinis generis Euphrasiae persimilibus; bracteis femineis 8 mm. longis 10 mm. latis unifloris 13-dentatis, dentibus modice longis alternis brevioribus; calveis masculi segmentis 4 ovatis 0.5 mm. longis, feminei segmentis 3 ovatis ca. 1 mm. longis; ovario dense piloso; stylis viridibus bracteo exsertis 7 mm. longis multilacinuligeris. — Zacapa, Department of Zacapa, Guatemala, 24 January, 1905, C. C. Deam, no. 190 (type, in hb. Gray). A species near Watson's Acalupha multispicata, which has very similar fertile spikes.

Clusia quadrangula Bartlett, n. sp., arborea 5-6 m. alta ubique glabra; ramis modice crassis subteretibus; foliis coriaceis ovatis 3-4 cm. latis 7-11 cm. longis, apice basique acutis, petiolo quam limbo quintuplo brevioribus; nervis lateralibus numerosis parallelis utrinque prominulis inter se 1-2 mm. distantibus angulo ca. 45° a costa abeuntibus; inflorescentia terminali quam foliis superis duplo breviore ramosa, ramulis angulosis plerumque in florem unum brevipedicellatum terminantibus; bracteolis infimis semi-ovatis basi connatis, sequentibus (a sepalis non different) sepalisque 14-16 per paria decussatis coriaceis semi-ovatis cordatis dorso carinatis, collective obpyramidatis quadrangulis (ex quo nomen specificum); petalis 4 coriaceis late ovatis quam sepalis duplo longioribus; staminibus pernumerosis in receptaculo elevato valde concavo pentagono dense aggregatis liberis, omnibus antheriferis, filamentis perbrevibus paene nullis, antheris rimula longitudinali dehiscentibus, connectivis haud productis. Flores feminei ignoti. - Livingston, Department of Izabal, Guatemala, February 17, 1905, C. C. Deam, no. 56 (type, in hb. Gray). This Clusia has no obvious relationship with any heretofore described species. Until pistillate flowers are discovered it seems unwise to characterize a new section for its reception.

Following Engler's treatment of *Clusia* in Flora Brasiliensis, it is excluded from all the sections of the genus except § *Euclusia* by the character of the receptacle. From subsections *Oxystemon* and *Chlamy-doclusia* of § *Euclusia* it is excluded by the muticous connective, and from *Cochlanthera*, the sole remaining subsection, by the four petals and very numerous stamens.

Rinorea deflexiflora Bartlett, n. sp., fruticosa 2.5 m. alta dichotome ramosa glabra novellis inflorescentiisque puberulis exceptis; ramis gracilibus juventate brunneolis aetate albobrunneolis glabris; lenticellis numerosis albis; internodiis superioribus ca. 11 cm. longis; nodis modice incrassatis in gemmam floriferem terminantibus; foliis oppositis cuneato-ovatis 4-12 cm. latis 8-24 cm. longis remote serratis caudatoacuminatis basi angustatis subcordatis supra atroviridibus subtus pallidioribus; petiolis 2-4 mm. longis; stipulis subulato-lanceolatis 7 mm. longis; inflorescentiis ubique puberulis inter ramos dichotomiarum terminalibus simplicibus 6 cm. longis; floribus ca. 15 longipedicellatis nutantibus bracteatis; pedicellis gracilibus 6 mm. longis deflexis; bracteis 3, una pedicellum subtendente, duabus infra pedicelli mediam suboppositis; sepalis 5 aequalibus acutis extus puberulis margine ciliatis 2 mm. longis; petalis 5 aequalibus oblongis 5 mm. longis haud unquiculatis apice valde revolutis; staminibus 5 glabris 3.5 mm. longis basi haud connatis; filamentis 1.3 mm. longis, anticis ad basin in dorso glandulae oblongae 0.8 mm. longae adnatis; connectivis in squamam ovatam lacero-ciliatam antherae loculis dimidio longiorem productis; stylo glabro stamina superante; ovario dense piloso. — Livingston, Department of Izabal, Guatemala, February 18, 1905, C. C. Deam, no. 61 (type, in hb. Gray). Four species of Rinorea or Alsodeia are now definitely known from north of Panama. One of them, the Mexican plant described by Watson as Alsodeia parvifolia, is of very doubtful generic affinity. The other old species are Rinorea silvatica (Seem.) (). K. and Rinorea guatemalensis (Wats.) Bartlett, n. comb. (Alsodeia anatemalensis Wats., Proc. Am. Acad. xxi. 458). Points which distinguish R. deflexistora from the former are that in R. silvatica the spikes are nodding, the flowers are nearly sessile, and the sepals are almost as long as the petals. In R. guatemalensis the leaves are broadest at the middle and are acute at the base, as contrasted with the more cuneate, subcordate leaves of R. deflexitlora.

Hybanthus cymosus Bartlett, n. sp., fruticosus 3 m. altus; ramis gracilibus alato-angulatis glabratis supra straminellis subtus viridibus; internodiis foliis brevioribus; foliis alternis ovatis 2-4 cm. latis 4.5-8 cm. longis serrato-crenatis glabratis basi acutis subsessilibus, apice rotundato-obtusis; stipulis lineari-subulatis usque ad 2 mm. longis;

floribus in cymas racemosas 15-30-floras axillares terminalesve aggregatis; cymarum bracteis perparvis ovato-deltoideis albidis; pedunculis 3-8 mm. longis; pedicellis 5 mm. longis breviter supra basin articulatis; sepalis ca. 1.6 mm. longis puberulis subaequalibus; petalis glabris in fructu persistentibus, duobus posticis ovatis apice truncatis 2.4 mm. longis, duobus intermediis aequilongis subquadratis breviter apiculatis ad basin antrorsum brevi-auriculatis, antico 1.9 mm. longo trinervio inter mediam apicemque constricto, parte inferiore (ungue) ampulliformi, parte superiore (limbo) multo parviore suborbiculari apice bilobata; staminibus 2 mm. longis inter antheras connatis tubum formantibus, tribus posticis triangulo-appendiculatis, filamentis perbrevibus liberis, duobus anticis appendicibus connatis, filamentis extus ad basin glandulae late scutiformi adnatis, glandula gibbositati petali antici conformali, loculis duobus contiguis antherarum anticarum abortivis; stylo corolla paululo longiore; capsula glabra viridi 6 mm. diametro 9 mm. longa. — Gualan, Department of Zacapa, Guatemala, 19 January, 1905, C. C. Deam, no. 385 (type, in hb. Gray). A species well marked by the combination of alternate leaves, numerous cymose axillary inflorescences, and short lower petal. In general structure it is most closely allied to such South American species as Ionidium atropurpureum St. Hil. and I. Sprucei Eichl.

Ipomoea anisomeres Robinson & Bartlett, n. sp., volubilis; caule gracili lignescenti glabro subtereti 3-6 m. longitudine a cortice brunnescenti-griseo obtecto aetate papilloso-scabrato; foliis ovatis integris profunde sinu patenti cordatis acutiusculis vel subattenuatis et in apice emarginato cum nervo excurrenti apiculatis penninerviis 6-11 cm. longis 4-7 cm. latis utrinque glabris subtus pallidioribus: petiolo gracili glabro 3-5 cm. longo; pedunculis axillaribus solitariis 3.5-6 cm. longis in summa parte composite cymoso-ramosis; pedicellis 1.5-2 cm. longis modice gracilibus sursum plus minusve incrassatis glabris; sepali, glabris margine albis 2 exterioribus 1-3 mm. longis suborbicularibus obtusis vix herbaccis 3 interioribus 1 cm. longis ellipticis apice rotundatis; corolla late infundibuliformi alba vel praesertim in faucibus purpurascenti 6.5-7 cm. longa, limbo 4-5 cm. lato subintegro, faucibus 1 cm. diametro 3.5 cm longis cylindratis deorsum in tubum brevem (ca. 1 cm. longum) proprium angustatis; capsula ovoidea acuta 10-12 mm. longa glabra biloculari; seminibus 4 griseo-fuscis breviter pubescentibus.—Gualan, Department of Zacapa, Guatemala, 12-14 January, 1905, C. C. Deam, nos. 318 and 319 (types, in hb. Gray). This species appears to fall into § Inaequisepalae, as defined by Peter in Engl. & Prantl, Nat. Pflanzenf. iv. Ab. 3, 29. The specific name alludes to the strikingly unequal sepals.

Cordia truncatifolia Bartlett, n. sp., arborea 5-7 m. altitudine; ramulis 2-3 mm. erassis flexuosis juventate griseo-ferrugineis pubescentibus aetate griseis glabris ad nodos incrassatis; foliorum cicatricibus reniformibus vel in ramulis vetustioribus lunatis, interdum gemma accessoria inter cornua infra gemmam normalem praeditis; foliis late ovatis maximis infra mediam 5 cm. latis 7.5 cm. longis integerrimis vel apicem versus erenato-dentatis basi obtusis truncatis apice plerumque abrupte acutis supra scabris atroviridibus subtus velutinopubescentibus griseo-viridibus, petiolis quam 8 mm. brevioribus; cyma dichotoma pauciflora foliis breviore omnino ferrugineo-pubescenti; pedicellis gracilibus 2-7 mm. longis; calvee campanulato ca. 1 em. longo juventate 5 mm. diametro ad fructus maturitatem plus minusve inflato 5-nervato 5-laciniato, laciniis irregulariter angustodeltoideis; corolla alba (?) infundibuliformi 15 mm. longa extus intusque puberula usque ad mediam 5-lobata, tubo brevi, lobis rotundis 7 mm. latis; staminibus 5 baseis loborum vix attingentibus, filamentis 5 mm. longis; stylo stamina aequante apice bis bifido; drupa (immatura) ovoidea minute puberula mucronata calvee inclusa. — Zacapa, Department of Zacapa, Guatemala, January 23, 1905, C. C. Deam, no. 160 (type, in hb. Gray). In no. 160°, collected at the same locality, the flowers and foliage are greatly reduced in size, a variation no doubt purely ecological. The shape of the leaves, which are remarkably like those of Polygonum cuspidatum Sieb, et Zuce., suffices to distinguish Cordia truncatifolia from all other species of Schestenoides.

Russelia rugosa Robinson, n. sp., fruticosa; ramis ramulisque 6-angularibus tomentello-puberulis pallide griseis; internodiis 5-8 em. longis; foliis oppositis vel ternis late ovatis obtusiuseulis grosse crenato-serratis basi integerrimis cuneatis supra seabris valde rugosis atroviridibus subtus vix pallidioribus laxe reticulato-venosis breviter pubescentibus 5.5-8 em. longis 2.6-4.8 cm. latis, petiolo crassiuseulo 5 mm. longo supra canaliculato pubescenti; cymulis subsessilibus axillaribus verticellastros parvifloros formantibus; ealycis lobis lanceolato-linearibus angustissimis caudato-attenuatis sordide pubescentibus nigrescentibus 5-6 mm. longis; corolla tubiformi verisimiliter coccinea 11-12 mm. longa pubescenti; capsula ovoidea nigrescenti levi nitida 4 mm. longa. — Gualan, Department of Zacapa, Guatemala, alt. 128 m., 18 January, 1905, C. C. Deam, no. 183 (type, in hb. Gray). A species pretty well marked in the genus by its large and very rugose leaves.

Tetramerium gualanense Robinson & Bartlett, n. sp., suffruticosum 1 m. altum ramosum, novellis viscoso-pubescentibus; caulibus subquadrangularibus lilacino-griseis minute albido-maculatis maturitate subglabratis; foliis oppositis petiolatis membranaceis subconcoloribus scabriusculis ovatis acute subcaudateque acuminatis integerrimis, limbo 6-8 cm. longo 3.5-6 cm. lato pinnatim nervatis basi acutis in nervis sparse puberulis aetate glabratis cystolithis conspicuis instructis, petiolo 1.5-2.5 cm. longo gracili supra canaliculato puberulo subtus rotundato glabro; spicis subdensis 2.5-4.5 cm. longis 1.3 cm. crassis ramulos oppositos terminantibus; bracteis obovatis cuneatis integerrimis acutis 5-nerviis utrinque glanduloso-pubescentibus 1 cm. longis 5 mm. latis, basi attenuatis; bracteolis binis oblanceolatis acutis cymbiformibus 9-10 mm. longis basi attenuatis in latere altero usque ad mediam in altero vix supra basin connatis: calvee 5-partito, lobis anguste lanceolatis acutissimis apice hispidulis; corolla subaequaliter 4-partita alba 1.5 cm. longa glabra, lobis anguste oblongis obtusis ca. 9 mm. longis; staminibus 2 lobos corollae subaequantibus in summo tubo insertis; antherarum loculis 2 summo subaequi-altis basi loculo uno plus minusve calcarato; stylo clavato; stigmate bifido; capsula oboyata acuminata glabra valde compressa ca. 2 mm. longa ca. 2 mm. lata, stipite obcompresso 2 mm, longo; seminibus 2 lenticularibus fulvis 2.6 mm, longis in latere interiore glabriusculis in latere exteriore crispo-pubescentibus. — Gualan, Department of Zacapa, Guatemala, 18 January, 1905, C. C. Deam, no. 397 (type, in hb. Gray). In the form of its inflorescence and bracts this species approaches the members of the genus which have sometimes been separated as Henrya.

Isertia Deamii Bartlett, n. sp., arbor parva 5 m. alta; ramis ramulisque crassis inferne subteretibus superne obtuse quadrangulis sordide tomentosis; internodiis 4-5 cm. longis; foliis 20-30 cm. longis 8-11 cm. latis utrinque acutis supra glabris subtus griseo-tomentosis, petiolo limbis 10-plo breviore; stipulis 6-9 mm. longis triangulis persistentibus; inflorescentia foliis multo breviore paniculata ca. 10 cm. longa, ramulis tomentosis ascendentibus 7-20 mm. longis, pedicellis 2-5 mm. longis, bracteis bracteolisque triangulis parvis; calvee fuscato hemi-ellipsoidali truncato nec distincte dentato; corolla ca. 30 mm. longa coccinea extus, lobis limbi exceptis, tomentosa, lobis 7 mm. longis obtusatis extus glabris intus lanugine flavo tectis; staminibus 6 inclusis tubo adnatis, antheris circum stigmata connatis; stylo apice in ramulos sex ca. 6 mm. longos terminanti; bacca calyce coronata 6pyrena. — Puerto Barrios, Department of Izabal, Guatemala, 24 February, 1905, C. C. Deam, no. 48 (type, in hb. Gray). Deamii, the third Middle-American species of the genus, is not similar enough to either of the old species to be confused with them.

Liabum caducifolium Robinson & Bartlett, n. sp., fruticosum; caulibus teretibus striatulis griseo-fuscis glabris delapsu foliorum nudis, internodiis 6-8 em. longis; inflorescentiis laxe corymboso-pan-

iculatis, ramis oppositis nudis patentibus vel arcuato-ascendentibus multicapitulatis, bracteis lanceolatis utrinque acutis integerrimis graciliter petiolatis supra glabris subtus arachnoideo-tomentosis, petiolo planiusculo glanduloso-hispidulo; pedicellis filiformibus 1-5 mm. longis; capitulis discoideis 6-floris; involucri squamis 13 acutis ciliolatis exterioribus ovato-lanceolatis 1 mm. longis interioribus gradatim longioribus angustioribusque intimis linearibus vel lineari-lanceolatis 5 mm. longis; flosculorum omnium corollis 6.5 mm. longis gracilibus sursum gradatim ampliatis sine faucibus distinctis, dentibus limbi linearibus ad apicem obtusiusculum attenuatis; pappi setis biseriatis exterioribus brevibus paucis planiusculis interioribus ca. 40 capillaribus fulvescentibus sursum scabriusculis. Achaenia immatura. — Near Acapulco, Guerrero, Mexico, between October, 1894, and March, 1895, Dr. E. Palmer, no. 245 (type, in hb. Gray). This species belongs to § Andromachia, and is closely related to L. glabrum Hemsl., but it differs in its much looser corymbose-paniculate inflorescence, its shorter involucre, and much more attenuate involucral scales.

Liabum Deamii Robinson & Bartlett, n. sp., scandens 3-5 m. longum: caulibus anthesi delapsu foliorum ignotorum nudis subteretibus lanulosis albidis, internodiis 2-4 cm. longis, nodis crassiusculis; inflorescentiis ovoideis thyrsoideis multicapitulatis albido-lanuginosis 1-1.5 dm. longis 5-8 cm. diametro; bracteis petiolatis ovatis integris discoloribus supra leviter griseo-pubescentibus subtus albo-lanatis; ramulis 3-5-capituliferis: capitulis discoideis 6-floris subsessilibus vel brevissime pedicellatis; involucri squamis ca. 13 obtusis exterioribus ovatis ca. 2 mm. longis externe pubescentibus interioribus gradatim majoribus 3-4 mm. longis ovato-oblongis apicem versus pubescentibus; flosculis Q involucro longe exsertis, corollis glabris verisimiliter flavidulis 7 mm. longis, faucibus cylindratis tubum proprium graciliorem subaequantibus, dentibus limbi patentibus anguste lanceolatis acutissimis; achaeniis 2.5 mm. longis deorsum angustatis griseo-olivaceis modice compressis striatulis breviter pubescentibus: pappi setis 2-seriatis exterioribus paucis subpaleaceis 1-2 mm. longis interioribus ca. 50 capillaribus sursum minute scabratis ca. 6 mm. longis albidis. — Gualan, Department of Zacapa, Guatemala, C. C. Deam, no. 194 (type, in hb. Gray). This species clearly belongs to the § Andromachia, and appears to be nearest L. glabrum Hemsl., from which it may be distinguished, however, by its pubescence and much shorter involucre, the latter scarcely exceeding the achenes.

# IV. DIAGNOSES OF NEW SPERMATOPHYTES FROM MEXICO.

#### By M. L. Fernald.

Carex ciliaris Fernald, n. sp., laxe caespitosa, caudice duro; culmis duriusculis 4-5 dm. altis acute triquetris superne ciliatis; foliis quam culmo brevioribus lineari-attenuatis 2.5-3.5 mm. latis, nervis marginibusque ciliatis marginibus revolutis; spicis 3-5, terminali clavellata subsessili 1-1.5 cm. longa vel omnino mascula vel apice foeminea; squamis masculis lanceolato-attenuatis pallide brunneis; spicis foeminiis breviter oblongis 0.6-2 cm. longis 0.5 cm. crassis, superioribus approximatis, inferioribus remotis et a bractea inflorescentiam aequanti vel superanti subtentis; squamis foemineis anguste ovatis acuminatis media parte viridibus 3-costatis levibus marginibus pallidis; perigyniis viridescentibus squamas aequantibus vel superantibus 4 mm. longis ellipsoideo-triquetris, faciebus planis 3-5-nerviis, rostro breviter conicosubulato hyalino bidentato. — Oak woods, Lena Station, Hidalgo, Mexico, alt. 2530 m., 26 August, 1905, C. G. Pringle, no. 10,039 (type, in hb. Gray). Nearest related, apparently, to C. anistostachys Liebm., which, according to the description, has scabrous culms, the staminate scales red-punctate, and the pistillate scales ciliolate.

Carex perlonga Fernald, n. sp., culmis 6 dm. altis laevissimis basi a vaginis ferrugineis tectis; foliis quam culmo plerumque brevioribus 4–5 mm. latis valde 1–3-nerviis serrulatis basi ferrugineis; bracteis inferioribus elongatis quam culmo longioribus, superioribus abbreviatis setaceis; spicis 7 solitariis inferioribus remotis superioribus approximatis laxe ascendentibus vel pendulis lineari-cylindricis 5–10 cm. longis 3–4 mm. latis apice masculis; squama mascula oblonga subacuminata fulva medio viridi, foeminea oblongo-lanceolata acuminata albo-fulva medio viridi; perigynio viridi trigono-fusiformi striato 4 mm. longo, ore obliquo subintegro. — Barranca below Trinidad Iron Works, Hidalgo, Mexico, alt. 1585 m., 2 June, 1904, C. G. Pringle, no. 8863 (type, in hb. Gray). A species of the Polystachyae, unique in its solitary not clustered spikes, thus closely approaching the Debiles.

Alnus firmifolia Fernald, n sp., arborea vel fruticosa 6-12 m. alta; ramis ramulisque atrobrunneis glabris cum lenticellis numerosis munitis; foliis elliptico-oblongis obtuse acuminatis vel apice rotundatis basi angustatis 5-17 cm. longis 2-5.5 cm. latis firmis duriusculisque supra glabris sublucidis subtus pallidis piloso-hispidis in nerviis prominentibus; petiolo crassiusculo glabro 0.7-1.2 cm. longo; inflorescentiis

fertilibus 6–9 cm. longis, amentis maturis 3–5 oblongo-cylindricis atrobrunneis pedunculatis 7–14 mm. longis 5–7 mm. diametro; nuculis cuneato-obovatis vel suborbicularibus rufobrunneis lucidis 1.5–2 mm. longis. — Mountains about Cima Station, Mexico, alt. about 3000 m., 30 August, 1905, C. G. Pringle, no. 10,040 (type, in hb. Gray). Resembling large-leaved A. jorullensis HBK., but quite lacking the close covering of waxy or granular atoms which characterizes the lower leaf-surface of that species.

Alnus Pringlei Fernald, n. sp., arbor parva; ramis ramulisque angulatis, juventissimis cinereo-puberulis mox glabratis; foliis late elliptico-ovatis 4.5–9 cm. longis 3–7 cm. latis apice breviter acuminatis basi rotundatis, marginibus regularibus vel paulo sinuatis crebre serrulatis, venis subtus prominentibus rufescentibus pilosis; petiolis 0.5–1 cm. longis piloso-ciliatis; ramis floriferis elongatis; amentis \$\mathcal{\chi}\$ 4–7 terminalibus anthesi 5–6 cm. longis; pedunculis fructiferis 2 valde divergentibus crassis; amentis \$\mathcal{\chi}\$ 3–4 sessilibus maturitate cylindricis 2.2–2.7 cm. longis 0.9–1.1 cm. diametro atrobrunneis; nuculis crassis late cuneatis et angulatis 2.5–3 nm. longis obscuris pallide brunneis. — By streams, near Uruapan, Michoacan, Mexico, alt. about 1525 m., 13 November, 1905, \$C. G. Pringle\$, no. 10,125 (type, in hb. Gray). Most nearly related to \$A. acuminata HBK., which has larger oblong-ovoid ashy-brown strobiles 1.5 cm. thick, and larger thick-winged lustrous nutlets.

Euphorbia Ariensis HBK., var. villicaulis Fernald, n. var. Eumecanthus Benthamianus Kl. & Garcke, in Kl. Tricocc. 42 (1860), not Euphorbia Benthami Hiern, Cat. Welw. Afr. Pl. i. 943 (1900). Euphorbia ariensis Benth., Pl. Hartw. 51, no. 387 (1840), not HBK. Nov. Gen. et Sp. ii. 57 (1817). Caulibus in parte inferiore valde villosis; foliis quam eis formae typicae aliquid latioribus; inflorescentia laxiore. — In pine forests at Coru Station, Michoacan, Mexico, alt. 1970 m., 29 October, 1905, C. G. Pringle, no. 10,116 (type, in hb. Gray). This locality is only about 48 km. to the west of Patzcuaro, which was Hartweg's original station.

Heliotropium calcicola Fernald, n. sp., frutex gracilis 6-15 dm. altus; cortice brunneo exfolianti; ramulis albido-strigoso-puberulis; foliis lanceolatis utroque attenuatis breviter petiolatis apice mucronatis cum pilis minutis et lucidis utrinque obtectis 2-4.5 cm. longis 3-10 mm. latis margine revolutis; spicis terminalibus et lateralibus geminis 0.5, maturitate usque ad 2, cm. longis; pedunculis gracilibus 1.3-2 cm. longis canescentibus; calyce 1.5-2.5 cm. longo cum pilis minutis adpressis canescenti, lobis lanceolatis; corolla anguste urceolata 3 mm. longa adpresse setulosa, lobis ovatis acuminatis; stylo nullo;

nuculis subglobosis 1.3 mm. altis albidis adpressé setulosis.—Limestone cliffs, Iguala Cañon, Guerrero, Mexico, alt. 760 m., 28 September, 1905, C. G. Pringle, no. 10,062 (type, in hb. Gray). Not closely related to other Mexican species, perhaps nearest H. coriaceum Lehm., which is much coarser, densely villous, with broader rugose villous leaves and larger flowers and fruits.

Salvia hisfanica L., var. chionocalyx Fernald, n. var., foliis bracteisque supra viridibus et minute pubescentibus subtus paulo pallidioribus et praesertim in nerviis breviter pilosis; spicis pertenuibus 5–10 cm. longis 1–1.5 cm. crassis; floribus adpresse ascendentibus; calycibus conspicue denseque albo-pubescentibus.— Fields, Uruapan, Michoacan, Mexico, 16 October, 1904, C. G. Pringle, no. 8837½ (type, in hb. Gray). A striking extreme of S. hispanica, the typical form of which differs in its ordinarily thicker spikes of less appressed cinereous calyces.

Salvia Hispanica L., var. intonsa Fernald, n. var., foliis et partibus superioribus caulis tomentosis; spicis brevibus crassis 1.5-5.5 cm. longis 1.5-2 cm. erassis; calycibus tomentosis patentibus. — Buena Vista, Department of Santa Rosa, Guatemala, alt. 1680 m., December, 1892, Heyde & Lux, no. 4401, in exsice J. D. Smith. Differing from S. hispanica in the dense tomentum of its leaves, stems, and calyces.

Salvia (Vulgares) mucidiflora Fernald, n. sp., herbacea (?) alta; caule cinereo-pulverulento obtuse angulato faciebus profunde sulcato; foliis rhomboideo-ovatis 3.5-10 cm. longis crenato-serratis subtus albidis et tomento brevi densoque obtectis supra griseo-viridibus cum pilis brevibus albis, basi cuneato integro in petiolum puberulum gradatim angustato; ramis brevibus patentibus; racemis laxis 3.5-10 cm. longis; rhachi et pedicellis et etiam calyce dense albovillosis paene lanatis; verticellis 3-6-floris subdistantibus; bracteis late ovatis mucronatis 4-7 mm. longis subpersistentibus laxe albo-villosis; pedicellis 1-3 mm. longis; calvee anguste campanulato anthesi 7 mm. fructifero 8-9 mm. longo. labio superiore acuminato ascendenti, inferiore rectiusculo cum lobis 2 deltoideis aristatis; corolla azurea et alba 13-14 mm. longa, labio superiore villoso oblongo 6 mm. longo, inferiore violaceo patenti paulo longiore; stylo villoso. — San Ramón, Durango, Mexico, 21 April-18 May, 1906, Edw. Palmer, no. 187 (type, in hb. Gray). Nearest related to S. longispicata Mart. & Gal. but differing in its crenate-serrate leaves and the long pubescence of the inflorescence.

Salvia (Vulgares) arthrocoma Fernald, n. sp., caulibus superne pilosis, pilis pallidis nodulosis; foliis rhomboideo-ovatis 4-8 cm. lougis supra basin cuneatam crenato-serratis apice acuminatis supra pilis compressis adpresse setulosis et in venis pilis gracilibus nodulosis mu-

nitis subtus in venis venulisque pilis gracilibus nodulosis pubescentibus; petiolis gracilibus 1.5-4 cm. longis; racemo brevi, rhachi a pilis nodulosis peculiaribus tecta; verticellis 3-6-floris demum 1-1.5 cm. distantibus; bracteis late ovatis longe acuminatis et calycibus in nervis marginibusque pilis gracilibus nodulosis munitis; pedicellis 3 vel usque ad 5 mm. longis; calyce campanulato anthesi 5 fructifero 8 mm. longo tubo valde costato, labiis deltoideo-acuminatis valde patentibus superiore ascendenti 2-3 mm. longo quam lobo recto inferioris breviore; corolla 1 cm. longa, tubo faucibusque albidis, labiis obtusis ringentibus apicem versus purpureo-tinctis, galea pilosa 4 mm. longa labium inferius latius paulo superante. — Barranca below Trinidad Iron Works, Hidalgo, Mexico, alt. 1620 m., 16 July, 1904, C. G. Pringle, no. 8940 (type, in hb. Gray). Somewhat suggesting S. fluciatilis Fernald, but clearly characterized by its slender jointed hairs.

Salvia (Vulgares) Lozani Fernald, n. sp., canlibus herbaceis gracilibus decumbentibus basi saepissime radicantibus aliquid ascendentibus demum 5-6 cm. longis minute glanduloso-setulosis, pilis patentibus; foliis regulariter remotis, jugis 4-6 cm. distantibus, foliis infimis suborbicularibus 1.2-1.6 cm. longis superioribus ovatis vel oblongis 1.5-2.5 cm. longis integris margine paulo revolutis basi rotundatis vel subcordatis apice rotundatis supra viridibus glabris pallide nervatis subtus pallidioribus et glandulis atrorubris punctatis; pedunculo 4.5-7 cm. longo; verticellis 3 remotis 2-floris; bracteis ovatis obtuse acuminatis glanduloso-setulosis 2-3 mm. longis; pedicellis 1-2 mm. longis; calvee anthesi campanulato glanduloso-setuloso rubropunctato 4-5 mm. longo, labio superiore obtuso 2-dentato nigrescenti 2 mm. longo, inferiore pallidiore lato brevissimo; corolla 17-18 mm. longa, tubo infundibuliforme leviter ventricosa 8 mm. vel ultra longo, galea breviter pubescenti 3-4 mm. longa, labio inferiore cyaneo albo-maculato 1 cm. longo, lobo medio 12 mm. lato. — Wet grassy places in pine forests near Trinidad Iron Works, Hidalgo, Mexico, alt. 1770 m., July-August, 1904, C. G. Pringle, no. 8928 (type, in hb. Gray). Named for Filemon L. Lozano, for several seasons Mr. Pringle's able field com-A unique species, nearest related perhaps to S. villosa panion. Fernald.

Salvia (Candicantes) chionophylla Fernald, n. sp., fruticosa depressa; ramis laxis gracilibus prostratis 3-6 dm. longis; cortice pallide brunneo pilis brevissimis crebris stellatis canescenti; foliis elliptico-ovatis vel breviter oblongis integris vel obscure crenatis utroque angustatis 0.5-1.5 cm. longis cinereis dense stellato-puberulis juventate canescentibus; petiolis gracilibus 2-4 mm. longis; racemis 0.5-1 dm. longis; verticellis 3-6-floris demum 2-2.5 cm. distantibus; pedicellis

2–4 mm. longis; calyce tubuloso-campanulato anthesi 6–7 fructifero 8–9 mm. longo valde costato, tubo lobis latis obtusis breviter acuminatis duplo longiore; corolla 1.5 cm. longa, tubo paulo exserto; galea azurea et alba pilosa 6 mm. longa a labio inferiore cyaneo superata. — On shelving rocks and gravelly slopes of the cañon-wall, Chojo Grande, Coahuila, Mexico, 29 August, 1904, Edw. Palmer, no 368 (type, in hb. Gray). Nearest related to the upright narrow-leaved S. thymoides Benth., which has a glandular calyx.

Salvia (Scorodoniae) chalarothyrsa Fernald, n. sp., ramis gracilibus retrorse molliterque pilosis; foliis cordato-ovatis acuminatis dentatis superioribus 2.5-4.5 cm. longis 2-3.5 cm. latis vix rugosis utrinque adpresse pubescentibus, pilis planis; petiolis 0.5-1.5 cm. longis dense pilosis; inflorescentia cylindrica laxe thyrsoidea 1.5-6 dm. longa; rhachi necnon pedunculis pedicellisque cum pilis mollibus patentibus glanduloso-capitulatis tectis: cymis 3-10-floris usque ad 3-4 cm. distantibus, pedunculis 0.5-2 cm. longis; bracteis lanceolatis vel linearibus tarde deciduis; calyce pedicellos aequante anguste campanulato anthesi 4 fructifero 5-6 mm. longo glanduloso-hirsuto, lobis alte deltoideis subaequalibus apice subulatis; corolla cyanea 12-13 mm. longa, tubo pallido glanduloso-punctato paulo exserto, galea brevissima breviter pilosa, labio inferiore multo longiore, lobo intermedio magno emarginato 7-9 mm. lato. — Hills about Tuxpan, Jalisco, Mexico, alt. 1220 m., 27 October, 1904, C. G. Pringle, no. 8856 (type, in hb. Gray). A remarkable species in its thyrsiform inflorescence, related only to S. thyrsittora Benth, a species also from the Jalisco mountains, from Tepic to western Michoacan.

Salvia (Inflatae) muralis Fernald, n. sp., fruticosa 1-2 m. alta; ramis gracilibus firmis subteretibus cinereo-puberulis; foliis anguste ovatis 6-9.5 cm. longis 2-4.7 cm. latis remote crenato-dentatis obtuse acuminatis basi subcuneatis vel rotundatis supra pallide viridibus adpresse setulosis subtus pallidioribus et glanduloso-punctatis dense albo-pilosis in costa media et in nervis principalibus; petiolo gracili cinereo-puberulo 2-3 cm. longo; ramis floriferis gracilibus brevibus ex axillis superioribus inferne foliatis; floribus saepissime geminis; pedicellis gracilibus 3-5 cm. longis; calyce anthesi curvato tubiformi 1.5-2 cm. longo inferne constricto viridique superne patente expanso et rubro-tincto sparse piloso, lobis deltoideis 5 mm. longis; corolla cinnabarina 4.5-6 cm. longa valde exserta pilosa tubulari-infundibuliformi, faucibus paulo gibbosis, galea pilosa 1.5-1.7 cm. longa labium inferius subaequante; staminibus styloque exsertis illo piloso. — Hanging from fissures in limestone-cliffs, Iguala Cañon, Guerrero, Mexico, alt. 762 m., 28 September, 1905, C. G. Pringle, no. 10,072 (type. in hb. xliii. - 5

Gray). Nearly related to S. pubescens Benth., which has a shorter, broader, and more colored calyx, shorter corolla, and nearly or quite glabrous style.

Salvia (Cyaneae) atrocaulis Fernald, n. sp., caulibus nigrescentibus vel purpurascentibus 1.8-2.4 m. altis basi 2-3 em. crassis in partibus inferioribus glabris inflorescentiam versus puberulis; foliis late cordato-ovatis utrinque viridibus supra sparse adpresso-setulosis et in nerviis puberulis subtus glabris sed glanduloso-punctatis regulariter dentato-serratis, limbo 7.5-15 em. longo 5-12 cm. lato apice caudatoacuminato; petiolo 4-14 cm. longo; inflorescentia racemosa 1.5-3 cm. vel ultra longa, rhachi puberula, verticellis 5-12-floris inter se denique 2-2.5 cm. disjunctis; pedicellis puberulis anthesi 7 mm. fructiferis 12 mm. longis; calyce anthesi 14 mm. fructifero 22 mm. longo glanduloso-punctato, in nervis cum pilis caducis moniliformibus pubescenti, lobis subulato-mucronatis deltoideis tubo anguste campanulato triplo brevioribus; corolla 5 em. longa violacea fere vel omnino glabra, tubo aliquid ventricoso labiis paulo longiore; stylo barbato. — Wet banks, barranea below Trinidad Iron Works, Hidalgo, Mexico, alt. 1650 m., 22 August, 1904, C. G. Pringle, no. 8887 (type, in hb. Gray). Nearest related to S. recurva Benth., but differing in its dark stems, broader firmer leaves, less pubescent ealyx, and essentially glabrous corolla.

Salvia (Gyaneae) flaccidifolia Fernald, n. sp., verisimiliter frutieosa; ramis gracilibus superne decussatim bifariam pilosis; foliis
graciliter petiolatis; petiolis supra pilosis inferioribus limbum superantibus; laminis ovatis cordatis caudato-attenuatis tenuissimis 3.5-9
cm. longis crenato-serratis supra atroviridibus adpresse setulosis subtus
pallide viridibus fere glabris in venis adpresse setulosis; racemis 6-8
cm. longis, verticellis 6-8 remotis 3-6-floris; bracteis ovatis aristatis
eaducis; pedicellis 2-5 mm. longis puberulis; calyce anthesi 5-6 mm.
longis, labio superiore ovato aristato inferiore bilobo biaristato; corolla
2-2.3 cm. longa eyaneo-purpurea, tubo valde ventricoso, labio superiore
recto 1 cm. longo, inferiore longiore pendulo valde dilatato. — Barranca
below Trinidad Iron Works, Hidalgo, Mexico, 1906, C. G. Pringle,
no. 10,298 (type, in hb. Gray). Nearly related to 8. recurva Benth.,
which it resembles in its very thin long-petioled leaves, but with much
smaller calyx and corolla.

Salvia (Tubiflorae) simulans Fernald, n. sp., caulibus glabris; ramis erectis brevibus; foliis ovatis abrupte acuminatis basi rotundatis vel rotundato-cuneatis regulariter dentato-serratis 0.5-1 dm. longis 3.2-6.5 cm. latis supra adpresse setulosis et resinoso-punctatis subtus glabris; petiolis paulo pilosis 4-8 cm. longis gracilibus; racemo principali 1.5 dm. longo; rhachi glanduloso-pulverula; verticellis 5-15-floris

demum 2 cm. distantibus; pedicellis gracilibus glanduloso-pruinosis 1.5 usque ad 7 mm. longis; calyce purpureo-tincto tubiformi anthesi 7–8 mm. fructifero 1 cm. longo, tubo basi valde costato pruinoso, faucibus paulo dilatatis levius costatis glabratis, labiis aristato-acuminatis 3–4 mm. longis inferiore bifido recto superiore sursum curvato; corolla rubro-purpurea 2.2–2.6 cm. longa, tubo et faucibus anguste cylindricis sursum curvatis 1.5–1.7 cm. longis 2–3 mm. diametro, labiis approximatis, galea dense pilosa labium inferius aequanti; stylo barbato. — Wet barranca below Trinidad Iron Works, Hidalgo, Mexico, alt. 1680 m., 22 August, 1904, C. G. Pringle, no. 8927 (type, in hb. Gray). Strongly suggesting S. Martensii Gal., which, however, has the ventricose corolla-tube of the Cyaneae. From that species, S. simulans, which has the cylindric corolla-tube of the Tubiflorae, is further distinguished by its rounded-cuneate leaf-bases, and especially by the elongate galea.

Castilleja Conzattii Fernald, n. sp., suffruticosa; caulibus simplicibus erectis glanduloso-puberulis; foliis linearibus vel lineari-lance-olatis 3–5-nerviis 2–7 cm. longis dense puberulis, inferioribus integris, superioribus pectinatis, laciniis linearibus patentibus; bracteis oblongis 1.5–2.5 cm. longis, summis coccineis trifidis, lobis lateralibus linearibus vel spatulatis, intermedio majore anguste obovato integro vel obsolete trilobo; pedicellis 1 mm. longis; calyce mediam tantum corollam paululo superante 1.5–1.8 cm. longo viridi et albo, antice et postice aequaliter fisso, lobis oblongis subtruncatis 5–6 mm. longis; corolla viridi et rubella 2.2–2.5 cm. longa, tubo 1.2–1.3 cm. longo, galea elongata, labii lobis obtusis 1 mm. longis. — Sta. Ines del Monte, Zimatlan, Oaxaca, Mexico, alt. 820 m., 8–9 December, 1905, C. Conzatti, no. 1360 (type, in hb. Gray). Nearest related, apparently, to the variable C. angustifolia (Nutt.) Don, of the northwestern United States, from which it differs chiefly in the broad middle lobe of the bracts.

Ruellia (Ophthalmacanthus) Pringlei Fernald, n. sp., fruticosa; ramis gracilibus flexuosis subteretibus glanduloso-villosis cinereis; foliis ovatis 3–10 cm. longis 1.5–4.3 cm. latis tenuibus utrinque molliter pubescentibus basi cuneatis apice longe attenuatis; petiolis gracilibus sublanatis 1.5–3.5 cm. longis; pedunculis 1.5–3 cm. longis cinereo-pubescentibus unifloris; bracteis lineari-spatulatis acutis 2.5–5 cm. longis; calyce 3–4 cm. longo, laciniis lineari-lanceolatis 2.3–3 cm. longis ciliatis; corolla alba 7–8 cm. longa anguste infundibuliformi valde exserta, limbi 5–6 cm. lati lobis breviter oblongis vel suborbicularibus retusis; capsula immatura angusta 2.5–3 cm. longa 7 mm. crassa glabra. — Hillsides, Balsas Station, Guerrero, Mexico, alt. 610 m., 27 September, 1905, C. G. Pringle, no. 10,071 (type, in lib. Gray).

Apparently nearest R. rosea (Nees) Hemsl., which is said, however, to have the obtuse leaves short-petioled, the stem angled, and the rose-colored corolla 2 inches long.

BIDENS ROSEA Sch. Bip., var. aequisquama Fernald, n. var., involucii squamis subaequalibus, eis seriei exterioris elongatis 5–8 mm. longis. — Thickets near Uruapan, Michoacan, Mexico, alt. 1525 m., 1 November, 1905, C. G. Pringle, no. 10,109 (type, in hb. Gray). Differing from B. rosea in the very elongate segments of the outer involucre, which in the original description of the species is said to be shorter than the inner, and which in herbarium specimens measures 2–4 mm. long.

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CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE, E. L. MARK, DIRECTOR.—No. 190.

MATURATION STAGES IN THE SPERMATOGENESIS OF VESPA MACULATA LINN.

BY E. L. MARK AND MANTON COPELAND.



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# MATURATION STAGES IN THE SPERMATOGENESIS OF VESPA MACULATA LINN.

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Received May 27, 1907.

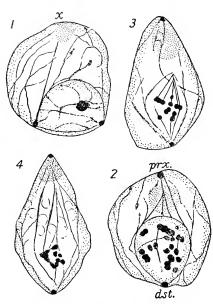
In a brief account of spermatogenesis in the honey bee, published four years ago, Meves (:03) showed that, contrary to the condition thus far observed in the animal kingdom generally, the maturation divisions of the primary spermatocytes resulted in the production of two "Richtungskörper" and a single functional cell, instead of four functional spermatozoa. The first of these two bodies was composed exclusively of cytoplasm; the second, however, was nucleated. Our observations on the germinal cells of the honey bee published last year (Mark and Copeland, :06) confirmed in a general way those of Meves, differing from his, however, in numerous details.

Meves states in a very few words in the paper cited that in the spermatogenesis of Vespa germanica the first maturation division results, as in the honey bee, in the formation of a non-nucleated bud of cytoplasm, but that the second gives rise to two cells of equal size, both of which are metamorphosed into spermatozoa.

Having been able to collect, prepare, and examine the male germinal cells of Vespa maculata Linn., we will set forth briefly in this paper some of our observations.

At the end of the growth period following the last spermatogonial division, the cells (compare Figure 1) closely resemble those of the honey bee. The nucleus is relatively large, and the chromatin is for the most part aggregated into a single, somewhat irregularly shaped body. Lying against the cell membrane are the remnants of the interzonal filaments of the preceding cell division, which have become metamorphosed into a rather homogeneous mass, to which we have given the name interzonal body (Figure 1, x).

As the spermatocyte enters the prophase of the first maturation division the centrosome, lying in contact with the cell membrane, divides, and the two daughter centrosomes move apart (Figure 1)



Figures 1-4. Primary spermatocytes. × 2800.

FIGURE 1. The two centrosomes moving apart; x, interzonal body.

FIGURE 2. Centrosomes at opposite poles of cell; nucleus showing chromosomes; prx., proximal centrosome; dst., distal centrosome.

FIGURE 3. First spindle figure with intranuclear spindle fibres.

Figure 4. Interzonal body at proximal pole, immediately before its abstriction; spindle figure disappearing, and extranuclear fibres prominent.

until they arrive at opposite poles of the cell (Figure 2). Although the centrosomes during their migration seem to influence to some degree the form of the cell, this modification in outline is not so prominent as in the honey bee. The nucleus continues to lie close to that one of the centrosomes which in the cells of the honey bee we have designated as the distal centrosome (Figure 2, dst.).

The stages immediately following this correspond strikingly to those of the honey bee. The chromatin, after passing through a spireme condition, gives rise to chromosomes which lie scattered irregularly through the nucleus (Figure 2). We have not as yet succeeded in determining the exact number of the chromosomes, but believe that it is not less than sixteen. nucleus now elongates, finally becoming more or less spindle shaped, but apparently fails to reach the proximal pole of the cell. Intranuclear spindle fibres staining in iron haema-

toxylin have meanwhile made their appearance, extending from the chromosomes first to the distal centrosome, and later in the opposite direction, to a region near the proximal end of the nucleus, it being now difficult to determine the exact extent of the nuclear membrane. Thus the proximal ends of the spindle fibres often appear to converge to a point at some distance from the corresponding centrosome (Figure

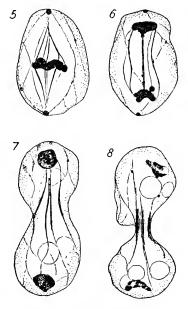
3); unlike the corresponding stage in the honey bee, there seems to be no evidence that these fibres connect with the proximal centrosome; however, numerous extranuclear fibres extend from the distal centrosome in the direction of the proximal one.

At this stage the interzonal body 5 already lies near the proximal centrosome.

The proximal end of the cell now elongates (Figure 4), and there is formed a small bud of cytoplasm containing the interzonal body and the proximal centrosome. This bud remains for a time connected with the cell by a neck-like process of cytoplasm, through which may be traced extranuclear fibres. This connecting process of cytoplasm becomes more and more attenuated until a complete detachment of the protoplasmic globule is effected.

This "Richtungskörper" consists chiefly of the interzonal body, but in most cases the interzonal body is surrounded by more of the unmodified cell protoplasm than exists in the corresponding globule of the honey bee. Like the latter, it contains no chromatin.

We have good evidence to show that the proximal centrosome divides, and that the two daughter centrosomes, in some cases, at least, move apart around the periphery of the globule. This migration may begin before the protoplasmic bud has become completely separated from the parent cell.



Figures 5-8. Spermatocytes after the abstriction of the interzonal body (i.e., secondary spermatocytes) × 2800.

FIGURE 5. Spindle figure of second maturation division in the beginning of the metaphase.

Figure 6. Anaphase of second maturation division.

FIGURE 7. Early telophase.
FIGURE 8. Late telophase. Spermatocyte nearly divided into two spermatids.

During the period of the abstriction of the interzonal body and accompanying cytoplasm, which closely resembles that of the honey bee, the development of the spindle figure is arrested, as in the bee, not being carried beyond the beginning of the metaphase. It is diffi-

cult to determine the fate of the chromosomes and spindle fibres at this time. The former appear to be aggregated to a greater or less extent, and their individuality seems thereby to be obscured.

After the formation of the non-nucleated "Richtungskörper" the chromatin is found to occupy the equator of the spindle, where it has regained the appearance of more or less distinct chromosomes. Thus is formed a fairly characteristic spindle figure in the metaphase (Figure 5). Division of the chromosomes now takes place, and the daughter chromosomes migrate toward the poles of the spindle, leaving stretched between them interzonal filaments (Figure 6). As the cell enters on the telophase it elongates, and a constriction is then formed at the equator (Figure 7). The constricting process is continued until the daughter cells remain connected to each other by only an attenuated neck of cytoplasm, through which can be traced the interzonal filaments. There result two spermatids, both apparently destined to become functional spermatozoa, for these cells, unlike the corresponding cells of the honey bee, are equal in size; they are immediately metamorphosed into spermatozoa.

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### THE PHYSIOLOGICAL BASIS OF ILLUMINATION.

BY LOUIS BELL.

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#### THE PHYSIOLOGICAL BASIS OF ILLUMINATION.

#### By Louis Bell.

Presented April 10, 1907. Received May 28, 1907.

The purpose of this paper is to point out that with the existing knowledge of physiological optics artificial illumination can be removed from the domain of empiricism and can be made to rest upon constants which have a definite physiological basis and which can be and have been predetermined with reasonable precision. For obvious reasons data which relate to the sensation of sight cannot rank with exact physical measurements, but they can nevertheless be evaluated closely enough to give a reliable basis of judgment in planning illumination to meet any given requirements.

Except for the aid received from accommodation and in binocular vision from convergence, we see things in virtue of their differences of color and of luminosity. Of these two the latter is by far the more important, particularly in distant vision. Objects of similar luminosity but differing considerably in color blend into the general view in a most astonishing fashion when at any considerable distance. Objects of similar color but of different luminosity also fuse into the general field, and if color and luminosity are both similar, things disappear in a way that is positively amazing. Small colored areas of moderate luminosity blend even at relatively short range, —a fact which the impressionists have turned to extremely good use, albeit they often transfer to canvas the color vagaries of the tired eye and the effects of simultaneous contrast rather than the fleeting impressions which they hold so precious. of Monet's landscapes, however, is wonderfully interesting from the standpoint of physiological optics, and especially in the existence of a critical distance, within which the picture loses its magic.

Practically, therefore, vision depends very largely upon the power of distinguishing differences of luminosity. And since objects in general are luminous only in virtue of light reflected from them, their visibility depends in turn upon their coefficients of reflection. So far at least as problems of artificial illumination are concerned, objects seen do not

range over a long scale of values of luminosity. Whatever the absolute values of the light reflected, the relative values expressed by the coefficients of reflection range from about 0.80 to about .01, very few substances returning more than the former or less than the latter percentage of the incident light.

The fundamental fact at the basis of vision is that the eye can perceive, within a very wide range of absolute intensity, a substantially constant fractional difference of luminosity. This is the purport of Fechner's law, and the fractional difference mentioned is well known as Fechner's fraction. Its numerical value for normal eyes and ordinary intensities of illumination is from .02 to .0055. The importance of this law in practical seeing is enormous, for in a room well lighted by diffuse daylight the illumination may vary from 100 meter-candles down to 10 or 20 in different parts of the room or at different times; and if power of discriminating difference of luminosity changed much with the illumination, one would be purblind most of the time. In some abnormal eves Fechner's fraction, with vision otherwise normal, is considerably increased, with serious results. A case is cited by Krenchel in which a patient was unable to get about in full daylight without stumbling over things. His condition was most puzzling until a test showed Fechner's fraction at a value of 0.1. At this value one could not distinguish between dark and light shades of brown and gray, having coefficients of diffuse reflection of say .15 and .25 respectively, and ordinary shadows on neutral surfaces would therefore disappear entirely. With Fechner's fraction at 0.5 no contrast less than that between white and very dark pigments would be easily distinguished.

Now while Fechner's fraction is fairly constant over a wide range of intensities, one easily realizes that as twilight deepens his power of discriminating shades is seriously impaired. It is this variation of Fechner's fraction with the illumination which determines the minimum amount of artificial (or natural) light which is effective in enabling one to see things en masse in their natural relations. For general vision any illumination above that required to bring Fechner's fraction for the normal eye up to its steady value is needless, and, as we shall presently see, may be injurious.

ently see, may be injurious.

Human vision, however, is frequently concerned with the observation of fine details both far and near, and the power of seeing these is within wide limits independent of the capacity of the eye for distinguishing small differences of luminosity. In the case mentioned by Krenchel this *visual acuity* was normal in spite of the extraordinary lack of sensitiveness to variations of light and shade. Acuity seems to depend on the structure of the retina and the quality of the eye as an optical in-

strument rather than on the direct or secondary sensitiveness of the nerve endings to stimulation by light. Great acuity is possibly commoner among savage peoples than in civilized races. König 1 has noted it among the Zulus, whose color vision, by the way, was normal; it has been found in unusual degree among the Kalmucks, and Johnson 2 noted it in the Congo peoples, in every case associated with slight hypermetropia. Some observations of Johnson (loc. cit.) would suggest that the extremely dark hue of the fundus oculi and consequent diminution of choroidal reflection found among the dark-skinned races may improve the definition, although perhaps at the expense of sensitiveness. It is of course well known that in the last resort the ability to separate objects like neighboring points and lines depends on the minute structure of the retina, and is greatest in the forea centralis, where the cones are most closely packed. The fovea too is well known to be somewhat less light sensitive than the retina in general. Using a wedge photometer, I find for my own eye that there is a difference somewhat exceeding one stellar magnitude between the foveal visibility and that outside.

Following out this line of investigation, it is not difficult to project the fovea as a dull spot in the field of view. Using a wedge photometer and fixing the eye at any point on a large sheet of white paper, one finds, on rather quickly cutting down the light by sliding the wedge, a roundish dark spot exactly in the axis and corresponding in diameter with the projection of the fovea. It is not easy to hold vision of this phenomenon since the axis of the eye inevitably tends to wander.

By drawing five rather faint crosses at the centre and corners of a square, say a decimeter on a side, one can, by careful manipulation of the wedge, make the central cross disappear in the foveal blind spot while the corner crosses remain visible. The facts regarding the independence of acuity and sensitiveness lend weight to the theory of our confrère Professor Lowell regarding the bearing of this matter on astronomical observations. Extreme acuity and extreme sensitiveness being both rather rare, any considerable degree of independence must render the coexistence of both in the same individual unusual in a very much higher degree.

The failure of acuity in a dim light is familiar, and its variation with intensity affords an independent criterion of the necessary requirements in artificial illumination. Enough light must be provided to bring the eye to its normal acuity as well as to its normal value of Fechner's fraction. Fortunately the researches of Dr. Uhthoff<sup>3</sup> and of Drs.

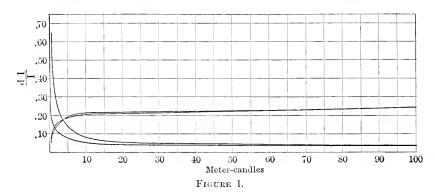
<sup>&</sup>lt;sup>1</sup> Nature, **31**, 476.

<sup>&</sup>lt;sup>2</sup> Phil. Trans., 194, B. 61

<sup>&</sup>lt;sup>3</sup> Graefe's Arch., **32**, 171; **36**, 33.

König and Brodhun<sup>4</sup> on acuity and Fechner's fraction respectively give us safe ground on which to travel in these respects.

In Figure 1 are shown the acuity curves and the shade-perception curves of the normal eye for intensities up to 100 meter-candles. Curves a and b give the values of Fechner's fraction for white light and deep crimson light ( $\lambda = 670 \,\mu\mu$ ) respectively, while c and d give the acuity curves for light orange ( $\lambda = 605 \,\mu\mu$ ) and yellowish green ( $\lambda = 575 \,\mu\mu$ ) respectively. The ordinates in the first case are  $\frac{dI}{I}$ , and in the latter case are in arbitrary units. The most important feature of these curves for the purpose in hand is that they are already becoming asymptotic at low values of the illumination, and except for strong colors at about



the same point. At about 10 meter-candles they have turned well toward the axis, and beyond 20 meter-candles the gain in shade-perception and acuity is very slow with further increase. Hence, when the light reaching the eye has risen to 10 to 20 meter-candles, further increase does very little in the way of assisting practical vision.

Artificial illumination can be safely based on this amount as a working intensity. Visual acuity is the controlling factor in most indoor lighting. It varies noticeably with color, but for practical reasons, which will appear later, the actual visibility of colored objects depends not on the differences here shown so much as upon their general light-reflecting power, which for dark hues is always low.

At great intensities both shade-perception and visual acuity considerably decrease, the former at roughly 25,000 to 50,000 meter-candles, the latter at much lower intensity. Neither function is likely to fail at any

<sup>4</sup> Sitz. Akad., Berlin, 1888.

intensity reached in the ordinary course of artificial lighting, though acuity may be seriously interfered with by dazzling and consequent rapid retinal exhaustion at intensities of a few hundred meter-candles, and the same secondary cause also impairs shade-perception long before its final decline.

It must be clearly understood that in specifying 10 or 20 metercandles as the intensity physiologically necessary to bring the eye into its normal working condition, these intensities are those which become visible to the eye, and not merely those that reach the objects under observation.

The light reflected from any object is Ik where I is the incident illumination and k the coefficient of reflection. Then, if  $\alpha$  is the normal illumination just indicated, the required incident illumination is

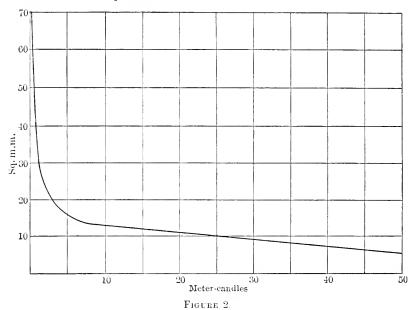
$$I = \frac{a}{\bar{k}}$$
.

Taking, for example, a = 15 meter-candles, and assuming that one is observing white or very light colored backgrounds for which k would have a mean value in the vicinity of 0.6, the value of I should be about 25 meter-candles. If the background is dark fabric for which k would not exceed 0.2, I would rise to 75 meter-candles, and for black fabrics one could hardly get too much light. A typical application of the principle may be taken in a draughting room where tracing has to be done, and the drawing must be well seen through the tracing cloth. for tracing cloth is about .35, and the illumination which makes the drawing visible is reflected from the drawing paper behind and passed back through the tracing cloth. The drawing paper probably reflects, if slightly off white, as is common, about 60 per cent of the incident light, and the final coefficient of the combination falls to about 0.25. Taking the same value of a as before, I = 60 meter-candles. Ordinary draughting rooms are found to be well lighted at this intensity. should be noted that draughtsmen generally use hard pencils, which make marks contrasting rather weakly with the paper, so that strong illumination is needed at all times.

In illumination out of doors, as upon the street, where no weak contrasts or fine details need to be made out,  $\alpha$  may be taken very much lower, but k is also low, and the minimum of about .25 or .30 meter-candle often allowed between lamps is, as the curves show, considerably too small for good seeing.

Effect of Pupillary Aperture. The iris serves as an automatic stop behind the cornea, adjusting itself so as to protect the retina from too violent changes of brilliancy. It may vary in diameter of aperture

from less than 1 mm. up to the full diameter of the visible iris, which in the darkness may retreat even within the rim of the cornea, as Du Bois-Reymond  $^5$  has shown. The eye therefore works over an aperture range varying from f20 or more down to f2.5 or f2. Incidentally the iris, acting as a stop behind the strongly refracting cornea, produces a certain amount of typical "pincushion distortion" which is evident in some optical illusions.



Data on the actual relation between intensity of incident light and pupillary aperture are scarce and imperfect. So much depends on the state of adaptation of the eye, individual sensitiveness, and probably also upon the intrinsic brightness of the source, that reliable values of the relation are difficult to obtain. From a reduction of Lambert's data, however, I have plotted the curve of Figure 2, giving as abscissae the illumination in meter-candles and as ordinates the area of the pupil in square millimeters. The striking fact is at once in evidence that this curve, like those of Figure 1, is rapidly becoming asymptotic in the neighborhood of 10 meter-candles. In other words, the contraction and expansion of the iris is less to protect the eye at high intensities

<sup>&</sup>lt;sup>5</sup> Centralbl. f. prakt. Augenheilkunde, 1888.

than to strengthen the retinal image at low intensities, even at the expense of considerably impaired definition. The human eye seems, however, to have become specialized for considerable acuity in a moderate light rather than for such extreme sensitiveness as is found in many nocturnal animals whose pupillary apertures vary over a much wider range than in man.

The curves of Figure 1 show simple retinal sensitiveness, and in reckoning from them one must at low illuminations take account of the gain from increased aperture. At ordinary working values of the illumination the gain is small, but at 1 or 2 meter-candles it is very material and plays a most important part in practical vision. For example, by curve a, Figure 1, an illumination of 0.5 meter-candle would imply a value of Fechner's fraction of about 0.2, which would in turn imply very much impaired shade-perception. In point of fact, one can see quite tolerably by a candle at the equivalent distance of 1.4 meters.

For if the pupil has adjusted itself to this situation the virtual illumination is that corresponding to about 2 meter-candles, the equivalent area of the pupil having increased to at least four times its ordinary value, which is that to which the curves of Figure 1 pertain. The result is a value of 0.1 or less for Fechner's fraction, which is quite another matter.

Were it not for this assistance, it would be quite impossible to get accurate photometric readings at the low intensities common upon the photometer screen. Similarly it would be exceeding difficult to get about at night, even by moonlight. In this latitude moonlight near full moon may fall to about 0.2 meter-candle, which would give Fechner's fraction at nearly .5, barring aid from the iris. With this aid increasing the aperture perhaps 6 times, one can see to get about very easily and can even read very large print. The same conditions have an important bearing on vision in presence of a strong radiant. For example, suppose that in a general illumination of 1 meter-candle one can

make out objects having a contrast  $\frac{dI}{I}$  = .15. Then let a light giving

20 meter-candles come fairly into the field of vision without materially illuminating these objects. The pupil will close to about one third its former area, giving a virtual illumination of about 0.3 meter-candles and a shade-perception of about .30, in which, of course, the objects disappear. Hence one cannot see well across a bright light, and even objects illuminated by it lose in visibility unless the change in illumination from them is greater than the concomitant change in aperture ratio.

The loss in visibility by the presence of a brilliant radiant in the field of view is increased by the change in adaptation of the eye. It is also probable that the intrinsic brilliancy of the radiant, as well as the light received from it, has a bearing on the pupillary aperture. Certainly at equal illuminations a well-shaded lamp gives higher visibility than a bare one, both being assumed to be in the field of view. There is therefore every reason for keeping such things as bare gas lights and electric lamps entirely out of the visual field, only admitting them thereto when they are so shaded as to keep the intrinsic brilliancy to low limits.

The eye has been evolved under conditions that imply rather moderate intrinsic brilliancy, admitting the general desire to keep the direct rays of the sun out of one's eyes. Sky light, of course, varies very widely in apparent intensity, being most intense in the presence of white cloud of moderate density. An average all the year round mean for the northern part of the United States, giving the intrinsic brilliancy of an aperture fully exposed to the upper sky, would be from measurements by Dr. Basquin, in the neighborhood of 0.4 candle power per square centimeter. This is lower than the intrinsic brilliancy of any flame, and approximates that of a bright lamp behind a thin opal shade. The ordinary window, which is in a wall rather than the roof, and gets its light largely from low altitudes and somewhat reduced by trees or buildings, is much less brilliant.

For instance, a window 1 m. wide and 2 m. high would be unusually effective if it gave 50 meter-candles at a point 5 m. within the room. This illumination would imply a virtual intensity of about 1250 candles at the window or an intrinsic brilliancy over the window area of 0.0625 candle power per square centimeter. Natural intrinsic brilliancies are decidedly low, and the chief difference between natural and artificial illumination, from the standpoint of wear and tear upon the visual organs, is the high intrinsic brilliancy of artificial light. If radiants are to be within the field of vision, they should be screened by diffusing globes or shades down to a maximum intrinsic brilliancy of preferably not above 0.1 or 0.2 candle power per square centimeter, certainly not above double these figures. As I have pointed out in a former paper, 7 if one plots the pupillary apertures as ordinates and the function  $\frac{1}{\sqrt{I}}$  as abscissae, the result is nearly a straight line, so that if one measures the visual usefulness u of a certain illumination

<sup>The Illuminating Engineer, Jan., 1907.
Trans. Ill. Eng. Soc., July, 1906.</sup> 

I in terms of what one may call the admittance of the pupil, then approximately

$$u = c \sqrt{I}$$

assuming that I is within ordinary ranges of intensity; that is, the eye works most efficiently at moderate illumination. The adverse factors in lowering the illumination are the optical errors introduced by increase of pupillary aperture and the general failure of shade-perception and acuity as the illumination falls below about 10 meter-candles. Spherical aberration and astigmatism increase rapidly at large apertures, so that definition of objects is much impaired. This doubtless plays its part in the failure of acuity in very poor light, although a more prominent fact is the increase of acuity as the eye is stopped down at illuminations considerably above the critical value at which the eye comes into normal working condition.

This critical value to which shade-perception, acuity, and pupillary reaction all point relates, it must be remembered, to the illumination received from the objects viewed considered as secondary light-sources. In too strong light thus received the eye is as seriously dazzled as if the source were a primary one, and the usual effects of after images and other evidences of retinal exhaustion and irritation at once appear. In very insufficient illumination there is failure to see contrast and detail, and there is an instinctive effort to push the eye near to the object at the risk of straining the mechanism of accommodation seriously. The familiar success of this expedient opens up some of the most curious questions of physiological optics.

Suppose, for instance, that one is viewing white letters on a dark ground. Evidently the letter acts as a secondary source of illumination, which proceeds from it, following the law of inverse squares. Now by halving the distance to the eye the intensity at the pupil is quadrupled, and at first thought one would infer that inspection of the shade-perception and acuity curves would give ample reason for the gain in visibility. But at half the distance the object subtends double the visual angle, and the retinal image is therefore quadrupled in area, leaving the luminous energy per unit of area the same as before; why, therefore, any gain in visibility? A similar question in a more aggravated form arises in accounting for improved vision through night glasses.

The key to the situation is found in the fact, put on a sound experimental basis by Dr. Charpentier, 8 that for the visible brightness of

<sup>8 &</sup>quot;La Lumière et les couleurs," p. 138 et seq.

objects giving images less than about 0.15 mm. in diameter the simple law of inverse squares holds. In other words, for weak stimuli at least, the visibility of small objects is determined by the total light emitted and by the distance and not by the surface brilliancy. It is as if a retinal area of about 0.15 mm. diameter acted as a visual unit, all stimuli acting upon this as a whole. As Charpentier (loc. cit.) puts the case with reference to distance, "In a word, the apparent brightness of a luminous object varies, other things being equal and within the limits indicated, in inverse ratio with the square of its distance from the eye."

As the eye then approaches a luminous object its apparent brightness increases, and it is distinguished more plainly so long as its image dimension is anywhere within the limit mentioned. As this corresponds to an object 2 mm. long at a distance of about 20 cm., the rule holds for reading type and the observation of small objects generally. The cause of this phenomenon is somewhat obscure. The natural supposition that it might well be due to spherical aberration and faulty accommodation in an eye with its pupil expanded, fails, as Charpentier (loc. cit.) shows, in two ways. First, the circle of diffusion in the eye due to spherical aberration is much smaller than the critical diameter in this case, and second, the phenomenon occurs when the eye is stopped by a diaphragm. I have tried it with a wedge photometer provided with a pair of 2 mm. apertures in line and separated by 6 mm., so that the ray pencil was of very narrow aperture, and find it still very conspicuous and apparently unchanged.

Charpentier and others are disposed to think its origin purely retinal, resulting from the spreading of the stimulus over retinal elements adjacent to those immediately concerned, and closely allied to the phenomenon of irradiation.

This latter phenomenon, however, is charged by Helmholtz largely to aberrations and dioptric faults generally. One of the best sources for studying irradiation is an incandescent lamp filament. At a distance of say 2 meters the apparent diameter of the filament at full incandescence is 4 or 5 mm. Using the wedge photometer upon it, the diminution of apparent diameter is at first rapid, until it falls to about 0.5 mm., at which it remains nearly constant until it completely vanishes. Stopping down the pencil of rays to 1 mm. or so cuts off most of the irradiation, but this seems to act in the main merely as a reduction of intensity, since the same effect is produced by a similar reduction in intensity by the wedge retaining the full aperture of about 5 mm. At a few hundredths of a meter-candle most of the irradiation has disappeared. The apparent breadth of the filament decreases without any

marked shading off at the edges, something as if a slit were being closed. The appearances indicate that beside the undoubted aberrations which come into play, there is considerable spreading of light in the retina at high intensities, reinforced very likely by reflection from the choroid, producing an effect quite analogous to the halation observed in a photographic plate.

The dimensions of the irradiation effect thus observed are inferior to the dimensions required by Charpentier, but it is quite probable that with a dark-adapted eye and feeble illumination, lessened contrast with the chief image would render the outlying portions more conspicuous.

The increased visibility of rather large areas is a still more puzzling matter, for which no satisfactory explanation has been produced. Inasmuch as all dealings like these with threshold sensibility have by this condition eliminated the cones of the retina from action, and depend upon rod vision entirely, it may be, since the rods are relatively more numerous away from the fovea, that mere size of image insures its falling on retinal areas relatively rich in active visual elements.

Aside from questions of intensity in artificial illumination is the matter of steadiness. It is of course well known that violent transitions of light and darkness, whether by moving the person or the eye, or by changing the intensity of the light itself, are distressing and injurious. The retina has a certain amount of visual inertia, which furnishes protection against very rapid changes, else one could not use lights successfully with alternating current. Flicker, from a practical standpoint, is troublesome about in direct proportion to its magnitude and in inverse proportion to its frequency. A change of intensity, however, covering some seconds, giving the iris plenty of time for readjustment, is hardly noticeable, while one of the same numerical magnitude, say 20 per cent each side of the mean, occurring once or a few times per second, is most painful. Ordinary incandescent lamps run on alternating current vary from 5 to 15 per cent on each side of the mean, according to the thermal inertia of the filament, and the frequency. With lamps of ordinary voltage and candle power the flickering is perceptible at between 20 and 30 cycles per second, the new high-efficiency lamps being worse than the older ones. Practically all lighting is done at above 30 ~, and troublesome flickering comes only from the irregular fluctuations of bad service. It must not be forgotten that one can impress serious fluctuations of light on the retina by compelling the eye to confront great variations of illumination when it moves. No artificial light should be arranged so that it forces the eye to make sudden transitions from blackness to brilliancy. Figure 3 is given here as a horrible example of what should never be permitted. I am sorry

to say that it is from the catalogue of a maker of reflectors who should have known better. Note the blackness of the interior and the excessive brilliancy of the light on the work.

In this connection should be mentioned the trouble that may come from the glare of light reflected from white paper, a risk to which book-keepers are especially subject. I have been in counting rooms where I found every clerk with signs of bad eyes.

Much paper is too highly calendered, and from this cause gives a combination of regular and diffuse reflection. Obviously a mirror placed on one's desk would give at certain angles an image of the lamp

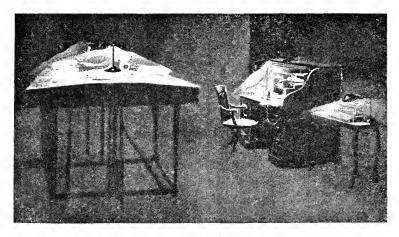
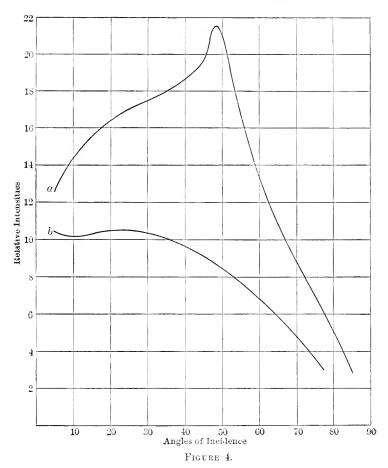


FIGURE 3.

of distressing brilliancy, and as the head might move this image would dodge into and out of the field of vision, giving an added cause of trouble. Glossy paper does somewhat the same thing. Figure 4 shows from Trotter's data  $^9$  the relative reflection at various angles of incidence from ordinary Bristol board (a) and from the nearly pure matte surface of freshly set plaster of Paris (b). The sharp peak corresponding to the angle of regular reflection is very striking. Light on a desk should therefore come from the side or rear rather than from the front, especially if the source is of high intrinsic brilliancy. For a similar reason the direction of illumination should be such as to free the eye from the effect of wavering shadows of the hand or head. The avoidance of shadow from the hand is the rationale of the sound old rule

<sup>9</sup> The Illuminating Engineer, 1, 488.

that the light should come from the left (left-handed people were forgotten). Shadows from the head and shoulders are much more troublesome, as they may exist to an annoying degree in rooms other-



wise well lighted, and they are in fact difficult to avoid in the general lighting of counting rooms and similar places.

Finally, one is nowadays often confronted by questions of color. Until electric lighting in its more recent forms appeared there was a sufficient similarity in the colors of artificial illuminants to place them substantially on a parity. At present, strong colors are common, and

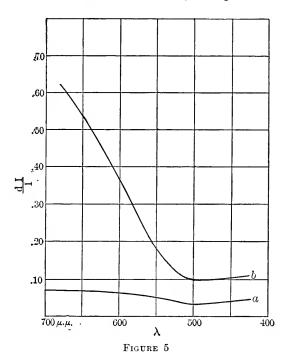
are likely to be increasingly so, since, as I have noted in a previous paper (loc. cit.), selective radiation is necessary to high luminous efficiency. One has to deal with the yellow of the flaming arc, the yellowish green of the Welsbach, the blue green of the mercury tube, and the violet of the enclosed arc, all of which may have to be compared with the deep orange of the Hefner lamp.

Practically the question of suitable color resolves itself into two parts, — first, the effect of color on the proper functioning of the visual apparatus, and second, its relation to our observation of colored objects. I shall not take up here the theories of color vision, save to note that many of their difficulties may now be charged to the existence of at least two kinds of independent visual elements, the rods and cones, differently distributed in the retina, and possessing two radically different types of visual sensitiveness. That the cones are highly evolved rods has been shown beyond much doubt by Cajal, and is in evidence in the simple rod structure found in the parietal eyes of some fishes and lizards and in lower organisms generally. Whether, as Mrs. Franklin <sup>10</sup> surmised, there are definite intermediate phases of sensitiveness between the achromatic vision of the rods and the full chromatic vision of the cones is an important topic for research.

May I venture to suggest that there are some reasons for thinking that there may even be a difference in kind between a simple photochemical rod stimulation and the strongly selective stimulation of the highly specialized cones? Selective activity does not necessarily connote chemical instability. They may coexist, as in some organic dyestuffs, or may be entirely independent, as in the fluorescence of heavy paraffin oils. The presence of strong pigmentation at the rods and its absence at the cones, coupled with the absence of visual purple in some nocturnal creatures whose eyes are presumably specialized for very weak light, suggests that the evolution of the retinal elements may have proceeded along more than one line. In fact, the Young-Helmholtz and Hering doctrines may find in a heterogeneous retina a certain amount of common ground. Be this as it may, mankind certainly has superimposed a very sensitive but achromatic rod vision, and a much less sensitive but chromatic cone vision, the latter being mainly central and the former mainly peripheral. The passage from predominant rod vision to predominant cone vision is shown in the sharp flexure of the curves in Figure 1. The exact point at which the color sensitive cones begin to get into action undoubtedly varies greatly in different eyes, and in the same eye in different conditions of adaptation.

<sup>10</sup> Mind, N. S., 2, 473 et seq.

illumination is progressively diminished, color vision gets more and more imperfect and uncertain, especially toward the red end of the spectrum. The effect is shown very clearly in the variation of Fechner's fraction with color as the intensity changes. Figure 5 shows the change in  $\frac{\partial I}{I}$  with  $\lambda$  for intensities of 15 meter-candles (a) and 0.75 meter-candles (b) respectively from the data obtained by König and Brodhun (loc.



cit.). Looking at the latter, it is evident that for the orange and red, vision must be very poor indeed, and in no part of the spectrum really good. In curve a color vision is pretty well established, although there are still traces of the point of inflection, which, as we shall presently see, falls near the point of maximum sensitiveness in very weak light, as if the superimposed rod vision were still helping out at this moderate intensity.

The Purkinje phenomenon, now well known to depend on the progressive failure of cone vision, also gives valuable evidence along the same line. It was noticed more than twenty years ago by Professor

Stokes <sup>11</sup> that the phenomenon varied with the areas involved, and recently Dow <sup>12</sup> has found that for small areas (*i. e.*, nearly central and hence mainly pure cone vision) Purkinje's phenomenon appears only below about 0.2 meter-candle. This figure would quite certainly have been somewhat higher had he used instead of red and signal-green glass the primary red and green, but it is clear from his results that the superposition of rod vision has a very considerable effect at moderate illuminations.

Finally, one must consider the luminosity curves at various intensities. Figure 6 gives in curve a the relative luminosities of the spectrum colors at fairly high intensity. The maximum is in the yellow, and the falling off, especially on the red side, is very rapid. This seems to be about the normal curve when the eye is fully in action. Curve b gives the luminosity curve for an intensity of about 0.0007 meter-candle. At this point color sensation is practically extinguished, and the maximum luminosity is perceptible, in what would seem the pure green were the light brighter, very near the E line and at a point corresponding to the inflection in the curves of Figure 5. This is practically the condition of pure rod vision. Curve c, Figure 6, lends confirmatory evidence. It is the luminosity curve obtained by Abney 13 from a patient with pure monochromatic vision. He had apparently an absolute central scotoma (cones atrophied rather than replaced by rods?), visual acuity greatly subnormal (central vision absent), and nyctalopia. This is a typical condition, nyctalopia being generally associated with central color scotoma, leaving peripheral vision but slightly affected (Fick). The patient apparently had no color perception, and his luminosity curve was practically identical with b, the normal curve for very weak light.

It would be most interesting to get proper tests for luminosity in one of the rare cases of congenital hemeralopia which would present the reverse condition of rods inactive and cones nearly normal. A comparison of such a case with luminosity in the hemeralopia associated with retinitis pigmentosa, in which peripheral vision is progressively contracted, might give valuable evidence as to the existence of retinal elements intermediate in function between rods and cones.

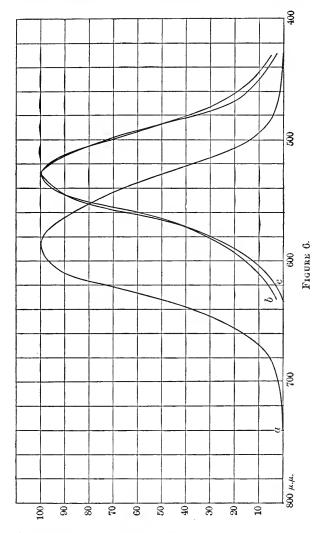
To sum up this phase of the matter, rod vision seems to be predominant from the very threshold illumination up to several tenths of a meter-candle, and to continue in force to all ordinary intensities, although rather easily exhausted. It gives low visual acuity and shade-perception perhaps of the order of a tenth normal, but, such as it is, it is our

Nature, 32, 537.

<sup>13</sup> Proc. Roy. Soc., 66, 179.

<sup>&</sup>lt;sup>12</sup> Phil. Mag., Aug., 1906.

main nocturnal reliance. Cone vision begins to come perceptibly into play at a few thousandths of a meter-candle, and at a few tenths is



pretty well established, but does not become normal over the visual area below five or ten meter-candles, and gains materially even beyond that, especially in acuity, which is weak at the lower intensities. Acuity in practical degree is chiefly an attribute of cone vision. The general theory of optical resolution requires acuity inversely as the wave-length of the light concerned. In practice this difference is in great measure masked by other and larger causes of variation. Chief among these is the very low luminosity of the shorter wave-lengths on the one hand and of the very long ones on the other. For example, in comparing acuity at  $\lambda = 500~\mu\mu$  and  $\lambda = 650~\mu\mu$  there is a proportional difference really due to color, but a ratio of 2.5:1 in luminosity in further favor of the green. Violet light favors acuity, if one can get enough of it, but a luminosity of .02 of the maximum in the yellow stands in the way.

Certain strongly colored lights, like the flaming calcium fluoride arc and the mercury arc, give apparently extremely sharp definition in black and white objects. In general this is not due to any advantage in color as such, but to improvement in the conditions of chromatic aberration in the eye. At rest for distant vision, the normal eye is in focus for the rays of maximum luminosity, and the focus for blue lies perhaps 0.4 mm. in front of the retina. That is, the eye is short-sighted for short rays. In near vision the rear conjugate focus moves backwards and the eve finds focus on the blue with less accommodation than usual. Thus Dow 14 finds that, while the mercury arc gives easy and sharp definition for near vision, at a distance of twenty feet or even less it becomes difficult to get focus. Lord Rayleigh 15 noticed some years ago that in very weak light he became myopic and required a glass of -1 diopter to restore normal vision. This effect is of the order of magnitude required by the shift of maximum luminosity into the green at very low intensities. Another phase of chromatic aberration is even more important. Were it not for the existence of a very high maximum in the luminosity curve, distinct vision would be impossible, since the difference of focus between the red and violet in the eye is something like 0.6 mm.; and were these extreme colors highly luminous, there would be no focal surface to which the eye could adjust itself. Only the great predominance of the central colors in luminosity gives the chance for a fairly sharp image.

It is easy to show the difficulties into which equal luminosity throughout the spectrum would plunge us. If one forms a grid of certain purples by cutting strips of tissue paper of the required color perhaps 5 mm. wide and 100 mm. long and pasting them upon a dark neutral background spaced about their width apart, one readily finds

The Illuminating Engineer, 2, 26 et seq.Nature, 31, 340.

the practical effect of chromatic aberration. From a distance of a couple of meters sharp definition of the grid is quite impossible. The purple chosen should give considerable absorption of the green, yellow, and orange, leaving strong red and blue evenly balanced in luminosity, and the background should be of not greatly different luminosity, so that the eye must rely mainly upon color effects. The rays from the grid are then of two widely different colors, for which the focal length of the eye differs. There are therefore two image surfaces of about equal intensity perhaps half a millimeter apart, and the effect is a curious blur, the eye hunting in vain for something definite upon which to focus.

Interposing now a deep red screen (concentrated saffronine is good), or a suitable blue screen, the image of the grid becomes nearly monochromatic and appears sharply defined. This is an extreme case, but any monochromatic light has an advantage in definition if other conditions are at all favorable. It seems highly probable that the well-known trouble found at twilight in trying to work by a mixture of natural and artificial light is due to a similar cause. The predominant hue of diffused sky light is strongly blue, while that of gas flames, incandescent lamps, and like sources, is strongly yellowish. At a certain point in the fading of daylight the luminosities of these widely different colors should balance closely enough to produce something of the effect just described, although the usual difference of direction in the two superimposed illuminations may play a part in the general unpleasant effect.

There is, however, an inherent danger in using monochromatic or strongly colored light for general purposes. Whatever may be the nature of color vision, a strongly colored light utilizes only a part of the visual apparatus. If of high intensity to make up for inherently low luminosity, it rapidly exhausts that part, and produces, as is well known, a temporary color blindness. There is at least a serious chance that long continued use of colored light would produce persistent and perhaps permanent damage to color perception. A light nearly white, with its maximum luminosity near the normal wave-length, runs the least chance of imposing abnormal strains on the visual apparatus.

In color discrimination the same rule holds good, for any considerable departure from white leads to entirely false color-values. In closing I may mention an interesting question which arises with reference to obtaining a light of high efficiency by building it up from the monochromatic primary components. Would the eye see clearly by such a light, and could it discriminate colors properly? The answer is probably yes. The equation for white is roughly

W = .20 R + .30 G + .50 B.

These are quantities as determined by slit width in the spectrum or a like process. There is sufficient predominance of luminosity in the green to avoid trouble from chromatic aberration, and the actual working of the combination in giving photographs in natural colors is such as to indicate proper color vision. As yet, however, no means are available for producing all three primary colors efficiently, and for white artificial light we are compelled to rely on what is in effect building up a nearly continuous spectrum from heterogeneous components, unless as usual we employ the continuous spectrum of an incandescent solid.



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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON THE DETERMINATION OF THE MAGNETIC BE-HAVIOR OF THE FINELY DIVIDED CORE OF AN ELECTROMAGNET WHILE A STEADY CURRENT IS BEING ESTABLISHED IN THE EXCITING COIL.

BY B. OSGOOD PEIRCE.



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BY B. OSGOOD PEIRCE.

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More than fifty years ago Helmholtz established, on theoretical grounds, the now familiar equations for the manner of growth of a current in a circuit of constant inductance under a given electromotive force, and proved by a brilliant series of experiments  $^{1}$  that the predictions of this theory were fulfilled in practice. It appeared, in particular, that if a circuit of resistance r containing a constant electromotive force, E, were closed at the origin of time, the current, I, would be given by the expression

$$\frac{E}{r}(1-e^{-\frac{rt}{L}}),\tag{1}$$

if L were the "potential of the circuit upon itself," that is, the self-inductance. The "induced current" (i) would satisfy the equation

$$i = \frac{L}{r} \cdot \frac{dI}{dt} = \frac{E}{r} \cdot e^{-\frac{rt}{L}}.$$
 (2)

If, therefore, I were plotted against the time, the resulting curve (OGQKC, Figure 1) would have as asymptote the straight line (ZC) parallel to the t axis at a distance E/r above it; the current in the circuit at any time (OP) would be given by the corresponding

<sup>&</sup>lt;sup>1</sup> F. E. Neumann, Abh. d. Berl. Akad. 1845 and 1847; Helmholtz, Die Erhaltung der Kraft, 1847; Pogg. Ann., 83, 1851; 91, 1854; Phil. Mag., 42, 1871.

ordinate (PQ) of the curve and the instantaneous value of the induced current by the distance (NQ) at that time, of the curve from the asymptote. The whole "amount" of the induced current up to the given time would be represented by the shaded area (A) shut in by the curve, the asymptote, and the ordinates, t=0, t=OP. If the electromotive force were suddenly shunted out of the circuit after the current had reached its final value, the "extra current" would have the value

$$\frac{E}{r} \cdot e^{-\frac{rt}{L}}.$$
 (3)

Helmholtz also studied the "forms" of the currents induced in the secondary circuit of a small induction coil at the making and breaking of the primary circuit, and, by using in the apparatus iron cores, some of which were solid and some finely divided, he showed that the effect of eddy currents in the iron upon the apparent duration of the induced currents might be very appreciable. The results of Helmholtz's experiments were confirmed with the aid of other apparatus, during the next thirty years, by a number of physicists.

The mathematical treatment of the subject begun by Neumann and Helmholtz was in 1854 pushed somewhat farther by Koosen, and in 1862 E. du Bois-Reymond published an elaborate discussion of the equations laid down by Helmholtz for the determination of the currents in two neighboring circuits of constant self-inductances  $(L_1, L_2)$  and constant mutual inductance (M), and gave the solutions of the simultaneous equations

$$L_1 \cdot \frac{dI_1}{dt} + M \cdot \frac{dI_2}{dt} + r_1 I_1 = E_1,$$

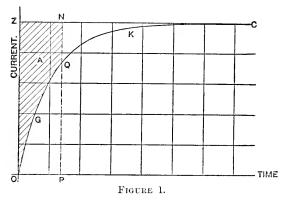
$$M \cdot \frac{dI_1}{dt} + L_2 \cdot \frac{dI_2}{dt} + r_2 I_2 = E_2,$$
(4)

corresponding to a number of different sets of physical conditions, in nearly the forms in which they now appear in textbooks. Du

<sup>&</sup>lt;sup>2</sup> Felici, Ann. de Chimie, **34**, 1852; N. Cimento, **3**, 1856; **9**, 1859; **12**, 1874; **13**, 1875. Cazin, Compt. Rend., **60**, 1865; Ann. de Chimie, **17**, 1869. Guillemin, Compt. Rend., **50**, 1860. Bertin, Mem. de la Soc. des Sc. Nat. Strasbourg, **6**, 1865. Bazzi and Corbianchi, N. Cimento, **4**, 1878. Bartolli, Mem. d. Acc. d. Lincei, **6**, 1882. Bazzi, Att. d. Acc. d. Lincei, **6**, 1882. Lemström, Pogg. Ann., **147**, 1872. V. Ettingshausen, Pogg. Ann., **159**, 1876.

<sup>&</sup>lt;sup>3</sup> Koosen, Pogg. Ann., 91, 1854. E. du Bois-Reymond, Monatsberichte d. Berl. Akad., 1861, 1862. Brillouin, Thèse, 1880; Jour. de Phys., 10, 1881; Compt. Rend., 1882.

Bois-Reymond showed that if the secondary circuit contained no battery, and if, after the primary current had been fully established, its circuit were suddenly broken, the current induced in the secondary circuit would have a form like that of the dotted curve (P) in Figure 2; if after a few seconds the primary circuit were again closed, the secondary current when plotted against the time would yield a curve either like Q or like S in the same diagram. The lines in this familiar figure have been drawn to scale for a certain pair of circuits the self-inductances of which are equal, fixed quantities and the resistances also fixed. Q, R, S correspond to three different values of the mutual inductance (M), which are respectively half as great, nine tenths as great, and equal to the self-inductance (L)



If the current is expressed in absolute units (absamperes) and the time in seconds, the shaded area represents the change in the total flux of magnetic induction through the circuit, during the time *OP*.

of either circuit. These curves show the currents induced in the secondary circuit when the primary is made; the crest of any such curve comes earlier the larger the value of M. The curve P, which represents a current induced in the secondary circuit when the primary circuit is broken, is drawn for the case  $M=\frac{1}{2}L$ , and therefore corresponds to the curve Q; E. du Bois-Reymond called attention to the fact that in such problems as this the areas V and W must be equal. The curves like P corresponding to R and S could be found merely by exaggerating all the ordinates of P in the ratio 9/5 or the ratio 2.

From the early days of induction coils, iron cores had been used to increase the mutual inductance of the circuits, and, soon after Helmholtz had given the equations for the currents in neighboring circuits of constant inductances, coils containing iron were studied from the point of view of the principles which he had laid down. Helmholtz's own experiments and those of others soon showed, however, that the introduction of masses of magnetic metal into the space within the coils complicated very much their action. It ap-

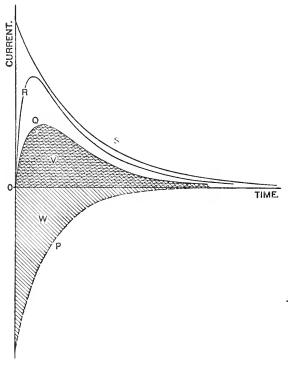


FIGURE 2.

The curves Q, R, S represent for different relative values of the mutual inductance the current induced in the secondary circuit of a certain induction coil without iron, when the primary circuit is suddenly closed.

peared that the existence of eddy currents in the iron, if the coil were solid, and the fact that the counter electromotive force in a circuit—as measured by the time rate of change of the flux of magnetic induction through it—is by no means proportional to the rate of change of the intensity of the current if a circuit "contains iron," made the simple theory of Helmholtz inapplicable, as he himself had foreseen

that it would be. The subject interested many investigators,<sup>4</sup> who found it easy to exhibit the disturbing effects of eddy currents in hindering rapid magnetic changes in solid masses of iron and in thus modifying the characters of the induced currents; but it was not until much work had been done by many persons on the phenomena attending magnetic induction in iron that the theory of the alternate current transformer which had meanwhile come to be of much practical importance was very well understood. With the general introduction of dynamo-electric machinery the magnetic behavior of the different kinds of iron used in its manufacture became of practical interest, and several different magnetometric and ballistic methods of studying permeability were invented and employed in making the necessary measurements upon relatively small pieces of the metal.

Soon after the first hysteresis diagrams had been obtained as a result of experiments either on comparatively thin iron or steel rings, or on long, fine wires, it was found by engineers that, on account of the considerable time required to establish a steady current in the coil of a large electromagnet to which a given electromotive force had been applied, the "reversed current," and even the "step-by-step" ballistic methods which had proved effective in the cases of slender toroids, were, in their old forms at least, not well fitted for studying the magnetic properties of such massive closed iron circuits as frequently occurred in practice. When there was a gap in such a circuit, the problem, of course, offered no difficulty,

<sup>4</sup> Faraday, Researches, 1831, 1832, 1846. Lenz, Pogg. Ann., 31, 1834. Henry, American Journal of Science, 1832; Phil. Mag., 16, 1840. Dove, Pogg. Ann., 43, 1838; 54, 1841; 56, 1842. Beetz, Pogg. Ann., 102, 1857; 105, 1858. Plücker, Pogg. Ann., 87, 52; 94, 1855. Rayleigh, Phil. Mag., 38, 1869; 39, 1870; 23, 1887; 22, 1886. Bichat, Ann. de l'École Norm., 10, 1873. Sinsteden, Pogg. Ann., 92, 1854. Magnus, Pogg. Ann., 38, 1836; 48, 1839. Schneebeli, Bull. de la Soc. des Sc. Nat. de Neufchatel, 11, 1877. Blaserna, Giornn. di Sc. Nat., 6, 1870. Maxwell, Electricity and Magnetism, 2, iv. Donati and Poloni, N. Cimento, 13, 1875. Stoletow, Phil. Mag., 45, 1873. Anerbach, Wied. Ann., 5, 1878. Rowland, Phil. Mag., 46, 1873; 48, 1874. Thomson, Phil. Trans., 165, 1875. J. Hopkinson, Phil. Trans., 176, 1885. Von Waltenhofen, Pogg. Ann., 120, 1863. Warburg, Wied. Ann., 13, 1881. Wiedemann, Lehre von der Elektricität. Ewing, Phil. Trans., 176, 1885; Proc. Roy. Soc., 1882, Magnetic Induction in Iron and other Metals. Du Bois, The Magnetic Circuit. Fleming, The Alternate Current Transformer. Ewing and Low. Proc. Royal Soc., 42, 1887; Phil. Trans., 180, 1889. Du Bois, Phil. Mag., 1890. Oberbeck, Wied. Ann., 22, 1884. J. and E. Hopkinson, Phil. Trans., 177, 1886. Jouanst, Compt. Rend., 139, 1904. E. Hopkinson, Brit. Assoc. Report, 1887. Tanakadaté, Phil. Mag., 1889. Wilson, Proc. Royal Soc., 62, 1898. Baily, Phil. Trans., 187, 1896. Many other references may be found in these sources.

but when large iron frames were completely closed, it became the custom, in satisfying commercial contracts, to attempt to get information about the permeability of the metal as a whole from tests, under given conditions, upon small, thin specimen pieces made as nearly as possible of the same material as the original, or else cut from it. was usually impossible, however, to be sure that the temper of the small piece was sufficiently like that of the mass to make it a fair representative of the whole, and the preparation of the specimens was often troublesome, so that some more practical method of procedure was seen to be desirable,5 and it seems to have occurred to a number of different persons independently that a good deal might be learned about the magnetic properties of the core of an electromagnet if one determined the manner of growth of a current in an exciting coil of a given number of turns wound closely about the core, when, under given initial conditions, a constant, known, electromotive force was applied to the coil circuit.

THE DETERMINATION OF SOME OF THE MAGNETIC PROPERTIES OF THE CORE OF AN ELECTROMAGNET FROM THE MARCH OF A CURRENT IN THE EXCITING COIL.

If, at any instant, the total flux of magnetic induction through the n turns of the exciting coil of an electromagnet is N (maxwells), if r is the resistance of the coil circuit (in ohms), i the current in it (in amperes), and E the applied electromotive force (in volts), then

$$E - \frac{1}{10^8} \cdot \frac{dN}{dt} = ri, \tag{5}$$

$$\frac{dN}{dt} = 10^8 \cdot r \left(\frac{E}{r} - i\right); \tag{6}$$

and if the final value (E/r) of the current be denoted by  $i_{\infty}$  and the change in N during the time interval  $t_1$  to  $t_2$  by  $N_{1,2}$ ,

$$N_{1,2} = r \cdot 10^8 \cdot \int_{t_1}^{t_2} (i_{\infty} - i) \, dt. \tag{7}$$

If, now, i be plotted against the time in a curve s (Figure 3) in which l centimeters parallel to the axis of abscissas represent one second, and an ordinate m centimeters long one ampere, the curve

<sup>&</sup>lt;sup>5</sup> Drysdale, Jour. Inst. Elec. Engineers, 31, 1901.

will have an asymptote, CY, parallel to the axis of abscissas, at a distance, KC, from it corresponding to E/r amperes, and, if OK represents the time  $t_1$ , and OL the time  $t_2$ , the area FGDC, or  $A_{1,2}$ , expressed in square centimeters, is equal to

$$lm \int_{t_1}^{t_2} (i_{\infty} - i) dt, \tag{8}$$

so that

$$N_{1,2} = \frac{r \cdot 10^3 \cdot A_{1,2}}{lm} = \frac{10^8 \cdot E \cdot A_{1,2}}{lm \cdot i_{\infty}}.$$
 (9)

In practice N usually differs from  $n \phi$ , where  $\phi$  is the induction flux through the iron core of the electromagnet alone, by only a small fraction of itself, and, if a is the area of the cross section of the core at any point, a certain average value of B, the induction, can be obtained from the expression N/na, though in such cores as are used in large transformers, H, and therefore B, would probably have very different values at different points of the section. Really N is greater than  $n \phi$  by the amount of the magnetic flux, in the air about the core, through the turns of the exciting coil, caused by the current in the coil itself or by neighboring currents, if there are such.

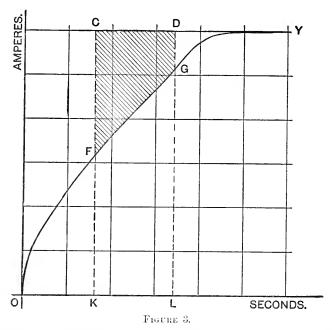
Using this theory, a good many persons have studied at various times the magnetic properties of different large masses of iron, and in 1893 Professor Thomas Gray of Terre Haute published in the Philosophical Transactions of the Royal Society a long series of very beautiful current curves, 6 obtained, with simple apparatus handled with great skill, from a 40 K. W. transformer belonging to the Rose Polytechnic Institute. A number of diagrams 7 showing the manner of growth of currents in the exciting coils of large electromagnets with solid cores have been printed within the last dozen years; of these the curves given by Dr. W. M. Thornton are especially interesting.

If to the coil of an electromagnet, in series with a rheostat of resistance r, a given electromotive force be applied, and if r be then reduced by steps, at intervals so long that one is sure that the final current belonging to each stage has been practically attained, the curve which has elapsed times for abscissas and the corresponding

<sup>&</sup>lt;sup>6</sup> T. Grav, Phil. Trans., **184**, 1893.

Hopkinson and Wilson, Journal of the Institute of Electrical Engineers, 24, 1895.
 Thornton, Electrical Engineer, 29, 1902; Phil. Mag., 8, 1904; Electrician, 1903.
 Peirce, These Proceedings, 41, 1906.
 Several figures from this last paper are here reproduced.

values of the strength of the current for ordinates, will have the general form of the line U in Figure 4, though, if the core be so large that the building up time at each stage is long, the diagram will be much drawn out horizontally. The curve which shows the march of the current when the electromotive force is applied directly to the coil without the intervention of the rheostat will resemble line V in the same figure. The exact forms of these curves depend, of course, upon

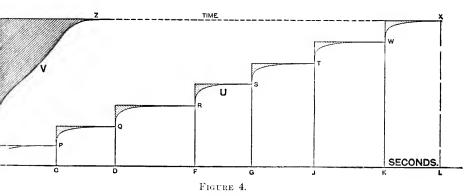


If l centimeters parallel to the horizontal axis represent one second, and an ordinate m centimeters long one ampere,  $A \cdot 10^8 \cdot r/lm$  (where A is the area, in square centimeters, of CDGF) represents the change in the magnetic flux through the circuit during the interval KL.

the magnetic state of the core at the outset, and will be very different if the iron has been thoroughly demagnetized before the observation is made, or if it be strongly magnetized. Figure 5, which illustrates this fact for some V curves, records some measurements made upon a 15 K.W. transformer (R) belonging to the Lawrence Scientific School. In the case represented by each line the core was previously magnetized in one direction with the full strength of the current, and the circuit was then broken and left open for a few seconds. With the

electromotive force in it unchanged in intensity, but in some instances changed in direction, the circuit was then closed again and a current curve obtained. If the electromotive force has its old direction, such a curve is said to be "direct"; if the new direction is the opposite of the old, the curve is called "reverse." In one case the magnetic journey of the core during the rise of the current is represented approximately by the portion PFM of the corresponding hysteresis diagram (Figure 6); in the other case the journey follows the arc QUZM. Lines 1, 2, and 4 in Figure 5 are reverse lines, while 3 and 5 are direct.

In Figure 4 the line OY corresponds to the final value  $(i_{\infty})$  of the current, and if its length in centimeters is  $m i_{\infty}$  and if A is the area in square centimeters shut in by OY, YX, and V, it is evident that in the



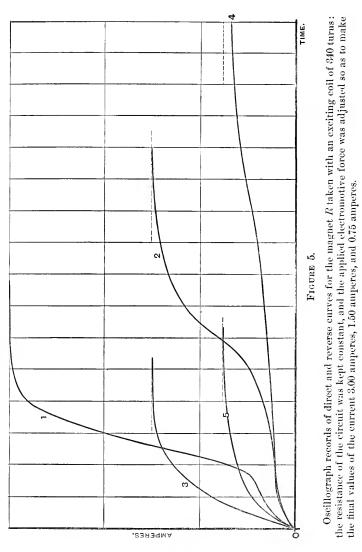
Curves which represent the growth of the current in the exciting coil of an electromagnet when (1), the circuit which has the resistance r, is closed and left to itself; and when (U), the circuit, is closed when it has a comparatively large resistance, which is then reduced to r by steps.

case represented by V the whole change in induction flux through the turns of the coil due to the current is

$$\frac{10^8 \cdot E \cdot A}{l \cdot OY}.$$

In the case represented by the line U,  $(10^8, E/l)$  times the sum of the terms formed by dividing each of the small shaded areas by the ordinate, expressed in centimeters, of its upper straight boundary, gives the change in the induction flux through the turns of the coil due to the current when it grows in the manner indicated. Of course if the

current is not allowed time to attain its final value at each stage, a serious error may be introduced.

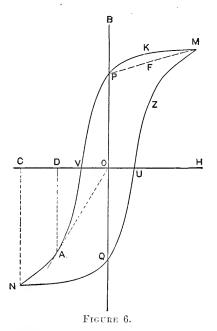


The amount of flux which, in a given large mass of iron, in a given magnetic condition at the outset, corresponds to a current of given final

strength in the exciting coil, usually depends in some slight degree upon the manner of growth of the current. If after a large core has been magnetized in one direction by the steady application of a given electromotive force until the current has reached its full value, the exciting circuit be broken, and, after the direction of the electromotive force

has been reversed, closed again, it sometimes happens that the magnetic flux after the new current has attained its maximum value is slightly less when the current follows the course of the curve V than when it grows by short stages in the manner indicated by the curve U. If, however, there are but two or three steps, the difference is, as a rule, of no practical importance, and if one has a suitable oscillograph or other recording instrument, it is possible to get a set of current curves for any given maximum value of the current from which an extremely good statical hysteresis diagram may be obtained for the core.

If while a steady current from a constant storage battery of voltage E is passing through the coil of an electromagnet, the resistance of the coil circuit be suddenly increased to a new value  $r_1$ , so that the current (i) will ultimately fall to a lower value represented by ON in



When a direct current curve is taken, the core of the electromagnet makes a magnetic journey represented approximately by the arc PFM; in the case of a reverse curve the core follows the line QUZM.

Figure 7, the current curve, which has been a horizontal line, sinks in such a manner as to become asymptotic to the horizontal line NB. At any instant after the change,

$$E - \frac{dN}{dt} = r_1 i, \tag{10}$$

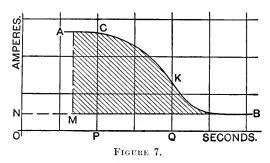
in absolute units, so that in volts, ohms, amperes, and maxwells,

$$N_{0.1} = 10^8 \int_{t_0}^{t_1} (E - r_1 i) dt = 10^8 \cdot r_1 \cdot \int_{t_0}^{t_1} (i_1 - i) dt.$$
 (11)

If an abscissa l centimeters long corresponds to one second, and an ordinate m centimeters represents one ampere, and if  $A_{0,1}$  stands for the area in square centimeters bounded by the current curve, the asymptote, and ordinates corresponding to the times  $t_0$ ,  $t_1$ , the change in the flux of magnetic induction through the circuit during this time-interval is (in maxwells)

$$\frac{10^8 \cdot r_1 \cdot A_{0,1}}{lm}.\tag{12}$$

If, after a current has been built up by stages in the coil of an electromagnet, in the manner indicated by curve U of Figure 4, the



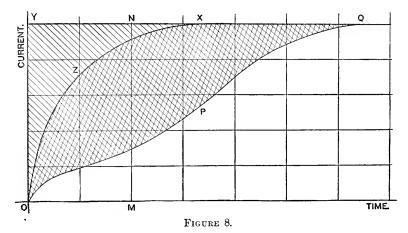
The shaded area represents on a certain scale the change in the flux of magnetic induction through a circuit when the resistance of the circuit is suddenly increased and then kept constant.

process be reversed, and the resistance of the circuit be increased by steps, the current curve will look very much as the curve U would if looked at from the wrong side of the paper when upside down.

As has already been stated, it is possible to get slightly different hysteresis diagrams for a massive core originally demagnetized, when the current is made to change from a given positive limit to the negative limit in different ways; and it is important, in predicting the behavior of a magnet which is to be used for a given purpose, to employ in computation the hysteresis diagram which corresponds to the particular magnetic journey which the core will take in practice. A single carefully made curve of the U type with a dozen steps will, however, give a result good enough for any commercial purpose, though

my own experience shows that it is not always easy to measure all the small areas, especially the lower ones, with the desirable accuracy, when the width (OY) of the whole diagram is only 12 or 14 centimeters.

If in the U diagram there is only one intermediate stage, and if the core is in a given magnetic condition at the outset, the change in the magnetic flux, due to a current of given final value, ought not to differ by more than perhaps a fraction of one per cent from the corresponding change when there is no intermediate step and the case is represented by V. Sometimes a series of U diagrams, each with but one



The areas between the asymptote and the curves Z and P are proportional to the changes of magnetic flux through the circuit caused by direct and reverse currents of the same final strength.

intermediate step, at a place determined by a proper choice of r, may be made to yield very accurate information about the permeability of the large mass of metal which will suit some special use of the magnet.

Figure 8, which resembles in general design some diagrams given by Dr. Thornton, shows a "direct curve" (Z) and a "reverse curve" (P) for a certain magnet. The area OZXY represents the change of magnetic induction when the core covers the are PFM (Figure 6) on the hysteresis diagram belonging to the journey; the area OPQXY represents the change of magnetic flux when the core takes the journey corresponding to the arc QUZM on the hysteresis diagram. The doubly shaded area represents the flux change corresponding to the line QUZMKP.

The Uses of Exploring Coils wound upon the Core of an Electromagnet.

If an electromagnet, in addition to its exciting coil, has another wound about its core, and if the observer has means of obtaining the intensity (i') of the current induced in this secondary coil, for given current changes in the exciting coil, as a function of the time, it is easy to study the magnetic properties of the core under the circumstances of the experiment. Let there be n' turns in the secondary coil, let the resistance of its circuit be r' ohms, and let N' be the total induction flux, in maxwells, through the turns of the coil at the time t, then if i' is measured in amperes

$$\frac{dN'}{dt} = -10^8 \cdot r' \cdot i'. \tag{13}$$

If i' be plotted against the time in a curve in which l' centimeters parallel to the axis of abscissas represent one second and an ordinate m' centimeters long one ampere, and if  $A'_{1,2}$  represents the area between the curve, the axis of abscissas and the ordinates corresponding to the time  $t_1$ , and  $t_2$ , we have in absolute value,

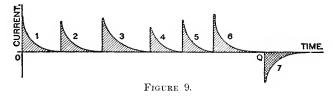
$$N_2' - N_1' = 10^8 \cdot r' \int_{t_1}^{t_2} i' \cdot dt = \frac{10^8 \cdot r' \cdot A'_{1,2}}{l'm'} = q' \cdot A'_{1,2}, \qquad (14)$$

where q' is a known constant.

When the primary current (i) in the exciting coil is growing, the current in the secondary coil has a direction opposite to that of i, and it is often desirable to emphasize this fact in a diagram by drawing the i, t and i', t curves on opposite sides of the axis of abscissas; but if the relative values of i and i' are alone to be considered, it is sometimes more convenient to disregard their relative directions. If in any case the current in the exciting coil of an electromagnet be made to grow in the manner indicated by curve U in Figure 4, the i', t diagram will consist (Figure 9) of a set of detached areas on the t axis. The sum of any number of these areas when multiplied by  $10^8 r'/l' m' n'$ gives approximately the whole change in the induction flux through the core up to the corresponding time, from the outset. In the "stepby-step" ballistic method of determining the permeability of a closed ring of rather small cross section the areas represented by the shaded portions of Figure 9 are determined by discharging the induced current through a calibrated ballistic galvanometer of long period, and assuming that the first elongations of the suspended system measure

these areas directly. As will appear in the sequel, it is possible, though not very easy, to get good results in this way, even if the cross-section of the laminated core is as great as, say, 800 square centimeters; for this, however, a properly constructed galvanometer is required.

The "time constant" of a circuit in which a current of given final intensity is to be established is shorter the higher the electromotive force used to generate the current; it is desirable, therefore, to employ a battery of rather high voltage and to reduce the current by non-inductively wound resistance in series with the exciting coil of the electromagnet. If a moving coil galvanometer is used, it is often necessary to correct for the effect of the counter electromotive force induced in the coil as it swings in the field of its own permanent magnet, and



A portion of the record of an oscillograph in the circuit of a secondary coil wound on the core of an electromagnet when the current in the exciting coil is made to change by sudden steps in the determination of a hysteresis cycle.

it is always necessary to use steps so short and to make the period of the galvanometer so long (perhaps 300 or 500 seconds) that the practical duration of the induced current may be small in comparison. It is usual to send the current to the exciting coil by means of a commutator and a long series of manganine resistance coils capable of carrying the desired currents; these coils are often mounted in a frame furnished with some device by which any or all of them can be shunted out of the circuit at pleasure. Two rheostats, made for this purpose some years ago by the Simplex Electric Company, have been found by the staff of the Jefferson Physical Laboratory very satisfactory in practice. By means of such a set of coils as those just described, one may easily get either a progressive, step-by-step increase or decrease in the current, or a reiteration of any particular step. One convenient way of arranging the apparatus for the repetition at pleasure of any desired step has been recently described by A. H. Taylor.<sup>8</sup> The method of rever-

<sup>8</sup> A. Hoyt Taylor, Phys. Rev., 23, 1906. Mordey and Hansard, Elect. Engineer, 34, 1904. Searle and Bedford, Phil. Trans., 198, 1902. Drysdale, Jour. Inst. Elect. Engineers, 31, 1901. Lamb and Walker, Electrical Review, 48, 1901.

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sals is usually unsatisfactory with large cores. A set of adjustable electrolytic resistances fitted for carrying heavy currents is often useful.

In the case of a very large closed electromagnet, even if the core be laminated, it is extremely difficult to get very useful results by aid of a ballistic galvanometer of short period, but if one has a suitable oscillograph or other recording instrument at hand, it is easy to obtain a diagram something like that shown in part in Figure 9, though it is necessary to make sure that the intervals between the steps, unlike those in this figure, are long enough to record the whole of each induced current.

If the primary current (i, t) curves are to be used in studying the magnetic changes in the core of an electromagnet, the sensitiveness of the oscillograph must be so adjusted that the deflection due to the largest value of the current (U, Figure 4) will make a record on the paper; if the (i', t) curves are to be used, the steps may be as numerous as one likes, and the sensitiveness of the recording instrument may be so great that, starting from the base line, the record of the highest induced current shall just fall on the drum. In this latter case the areas to be measured may be made so large that any uncertainty as to the exact time when any induced current may be considered to end is unimportant. When many records are taken on the same paper, the drum has an opportunity to revolve a good many times during the operation, and it is not always easy to decipher the complicated maze of curves. Of course the fact that an electromagnet has a closed secondary circuit modifies somewhat the form of the building-up curve in the primary, but, theoretically at least, this should not affect the value of the magnetic flux due to the primary current if its final intensity is given, and the difference is inappreciable if there are only a few turns in the secondary coil.

Instead of changing the resistance in the primary circuit suddenly, at each step, Dr. Thornton, in dealing with the frames of some very large dynamos, made each step gradually, by moving an electrode slowly in a trough of acidulated water from one stopping place to another. Figure 10 is a close copy of one of his records published in the "Philosophical Magazine" for 1904.

## FLUXMETERS AND QUANTOMETERS.

Given an amperemeter of the ordinary d'Arsonval type, in which an open-frame, low resistance, unshunted coil swings in the strong magnetic field between an interior soft iron core and the hollowed-out jaws of a powerful magnet, it is often possible to make the controlling

springs so weak that if the coil circuit be suddenly closed on itself while the coil is in motion, the damping effects of the induced currents will bring the coil almost instantly to rest wherever it may happen to be, and, until the circuit is broken, the coil will keep its position fairly well. Several years ago Dr. R. Beattie  $^9$  showed that if the ends of a low resistance exploring coil (A) be electrically connected with an instrument of this kind, and if the flux of magnetic induction through A be changed during the time interval T by an amount N, the coil will move from its initial position to a new position through an angle proportional to N and, apart from pivot friction, practically independent, within wide limits, of T.

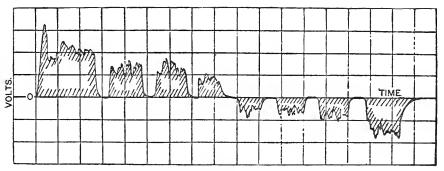


FIGURE 10.

Typical record for half a hysteresis loop, given by Dr. Thornton.

The "quantometer" first made by Dr. Beattie had a coil of twenty-four and a half turns wound on a metal frame and suspended on a single needle point between the poles of an electromagnet; the ends of the coil dipped into mercury cups fixed to the case of the instrument. In the kind of fluxmeter now common, the coil is hung by a silk fibre (or a quartz thread) from a spring, so as to avoid pivot friction; a permanent magnet is used, and the current is led into and out of the coil through helices of very fine silver or copper gimp; the resistance of this gimp is sometimes much greater than that of the coil itself, and for laboratory use it is often well to employ mercury cups, as Dr. Beattie did, so arranged as to minimize the disturbing effects of capillarity. The original quantometer had a resistance of only one ohm.

Many persons who have attempted to use very strong electromagnetic fields in d'Arsonval galvanometers have found that it is very difficult

<sup>&</sup>lt;sup>9</sup> R. Beattie, Electrician, Dec., 1902.

to procure insulated copper or silver wire for the suspended coil so free from paramagnetic properties that the coil shall not have a permanent "set" in the field, too strong to be conveniently controlled by the torsion of the gimp through which the current enters the coil. In the case of a quantometer where there is practically no controlling moment from the suspending fibre, the paramagnetic properties of the coil may be very troublesome; and in some of the most recent instruments the angular movements of the coils, due to given changes of induction through the turns of the exploring coils, are somewhat different according as the movement is towards the left or towards the right. a telescope and scale be set up in such a position that the behavior of the coil can be watched after it has moved through a considerable angle, urged by a sudden, definite change of flux in the exploring coil, it will often be found that the coil does not remain even approximately at rest, but moves steadily and so rapidly that a considerable error is introduced if the given change of flux through the exploring coil is made slowly. It is desirable, therefore, to test an instrument of this kind carefully before using it.

If great accuracy is not required, a good fluxmeter, of some standard make, and of sensitiveness suited to the work to be done, is, in experienced hands, a most useful instrument; the time needed to establish a current of given strength in the coil of a large electromagnet with a solid core may be several minutes, but a very good fluxmeter will, nevertheless, show directly, with an error of not more than 2 per cent, the change of magnetic flux through the core.

If the fluxmeter coil is not wound on a closed metal frame, the mutual damping effect of currents in the coil and in the core which it surrounds are not always effective unless the resistance of the external circuit, made up of the exploring coil and its leads, is fairly small compared with the resistance of the suspended coil itself. An instrument, therefore, which works very well with an exploring coil of a small number of turns often becomes quite useless when, in order to get the required sensitiveness, the observer tries to employ an exploring coil made of many turns of fine wire. On the other hand, if a fluxmeter of this kind is too sensitive for a given piece of work, it is not always easy to reduce the sensitiveness quickly.

If the flux changes to be measured are large, it is often convenient to have a fluxmeter the coil of which consists of a few turns either wound on a copper frame or else accompanied by several turns of stout wire closed on themselves. It is possible to use such an instrument with many different exploring coils and to change its sensitiveness within wide limits by varying the resistance of the external circuit.

In doing a small part of the work described below, I was able to use either a Grassot Portable Fluxmeter, or a certain fixed laboratory fluxmeter (F) furnished with a tall chimney to hold the 140 centimeter long fibre by which the coil was suspended. The cast-iron

magnet of this last mentioned instrument had, when finished, the form shown in plan in Figure 11 and was 45 mms, thick. The casting was made with a web connecting the poles, and this was removed after the hole for the coil had been cut out and finally reamed to a diameter of exactly 5 cms. on a Browne and Sharpe milling machine. The magnet was hardened and treated by Mr. G. W. Thompson, the mechanician of the Jefferson Physical Laboratory, who has had much experience in this kind of work. During the process the poles were held in position by an iron voke. The core (shaded in the diagram) within the coil is 41.3 mms. in outer diameter, and is about 7 mms. thick. The instrument was constructed and set up by Mr. John Coulson, who has helped me in countless ways during the progress of the work. It was

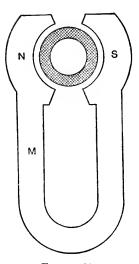


FIGURE 11.

Plan of one of the permanent magnets of the flux meter F; the shaded area represents the cross-section of the soft iron core.

comparatively easy to substitute one of the set of coils belonging to this fluxmeter for another. For certain purposes it was convenient to have a coil of 200 turns of stout insulated wire which was wound about the magnet, though the latter had a large permanent moment.

## THE COEFFICIENTS OF SELF-INDUCTION OF A CIRCUIT WHICH HAS AN IRON CORE.

When many years ago it was found that the induction B at a given point in a piece of iron exposed to a given magnetic field H is not only not in general proportional to the intensity of the exciting force, but is not even determined when H is given, it became evident that no such constant can exist in the case of an inductive circuit which "contains" a magnetic metal as was assumed in the conception of Neumann's

"Electrodynamisches Potential," <sup>10</sup> and that the different common definitions of self-induction, when applied to an electromagnet of the usual form, really describe physical quantities which are widely different from one another. The ambiguity in the use of the term "self-induction" still exists, and it will be convenient in this paper to adopt the notation used by Sumpner <sup>11</sup> in his article on "The Variations of the Coefficients of Induction." If, in absolute value, I is the strength of a current growing in the coil of an electromagnet with laminated core, if N is the total flux of magnetic induction through the turns of the coil, and e the counter electromotive force of induction, we may call the ratio of e to the time rate of change of the current,  $L_1$ , the ratio of N to the current,  $L_2$ , and the ratio, to  $I^2$ , of twice the contribution (I) made by the current to the energy when there are no other currents in the neighborhood,  $I_2$ , so that

$$e = L_1 \cdot \frac{dI}{dt}, \quad N = L_2 \cdot I, \qquad L_1 = \frac{dN}{dI}$$

$$e = \frac{d(L_2 \cdot I)}{dt}, \quad T = \frac{1}{2} L_3 \cdot I^2, \quad L_1 = L_2 + I \cdot \frac{dL_2}{dI}.$$
(15)

If then for a particular magnetic journey, taken at a given speed, N is given as a function of I in the form of a curve like OPQ in Figure 12, the value, at any point P on the curve, of  $L_1$  is the slope of the curve or the tangent of the angle XKP; the value of  $L_2$  at P is the slope of the line OP or the tangent of the angle XOP; the value of  $L_3$  is the ratio of twice the curvilinear area OPD to the area of the square erected on OJ. Similar definitions are sometimes given for such a magnetic journey as is represented by the line MGPQ of Figure 13.

In the paper just cited Sumpner gives a very interesting graphical method of constructing a curve which shall show the manner of growth of the current in the coil of the electromagnet when the curve which connects N and I is given.

## THE ELECTROMAGNETS USED IN DOING THE WORK DESCRIBED BELOW.

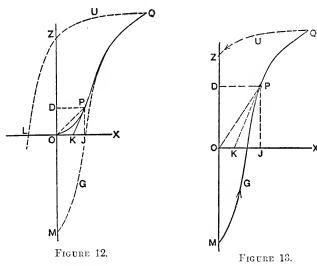
A number of electromagnets were used in carrying on the experimental work described in this paper.

Though the investigation had to do primarily with magnets the cores of which were laminated or otherwise finely divided so as to get

<sup>10</sup> Neumann, Abh. d. Berl. Akad., 1845.

<sup>&</sup>lt;sup>11</sup> Sumpner, Phil. Mag., **25**, 1888.

rid in great measure of the disturbing effects of eddy currents, one or two large magnets with massive cores were useful for purposes of comparison. One of these (P), which weighs about 1500 kilograms, has the general shape shown in Figure 14. The outside dimensions of the frame proper are about 101 cms.  $\times$  80 cms.  $\times$  40 cms. The base is of cast iron and of rectangular cross-section (20 cms.  $\times$  40 cms.), the cylindrical arms are of soft steel 25 cms. in diameter, the rectangular pole pieces are 4.5 cms. thick, and the area of each of the opposed



This illustrates different meanings of the word inductance.

faces is about 580 square centimeters. The four coils have together 2823 turns, and a resistance at 20° C. of about 12.4 ohms.

Figure 15 shows in outline the electromagnet Q, which weighs about 300 kilograms: the core has a square cross-section of about 156 square centimeters area, and is built up, cobhouse-fashion, of soft iron plates about one third of a millimeter thick, each of which was immersed in thin shellac and then thoroughly baked in an electric oven before it was used. Each of the spools, which are practically alike, weighs about 30 kilograms and has four coils, an inner one forming a single layer, the next forming three layers, and the two outer ones wound together side by side from two supply spools, and each equivalent to five layers; in all, both spools together have 3883 turns. The whole core frame is about 74 cms. long and 62 cms. broad. One stratum 2.5 cms. high

and reaching across the middle of the core (Figure 16 a) within one of the spools, is made up of five portions insulated from one another, and each of these is surrounded by an exploring coil of insulated wire.

Figure 16 b shows the form of the cross-section of the rectangular core frame of a 15 kilowatt transformer (R) constructed for experimental purposes and belonging to the Lawrence Scientific School. Besides a low-resistance primary coil, this transformer has 19 similar coils each of about 85 turns, any number of which may be connected to form a secondary circuit. The outside dimensions of the core frame are about 78 cms. and 34 cms.; the area of the cross-section of the finely divided core is about 108 square centimeters.

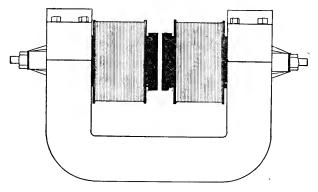


FIGURE 14.

The electromagnet P. This magnet has a solid core which weighs about 1500 kilograms.

Magnet S has a core consisting of two round solid pieces 76 cms. long and 7.4 cms. in diameter with axes 24 cms. apart, connected together at the ends (so as to form a rectangular frame) by two massive iron blocks. This magnet has two spools, each of which has two coils formed by winding two strands side by side; the whole number of turns is 1724.

The core of magnet T forms a square 58 cms. long on the outside and 53.5 cms. wide. Its cross-section is a rectangle 7.5 cms. by 6.7 cms. The core is built up of sheet metal 0.38 of a millimeter thick.

Through the kindness of Dr. George Ashley Campbell I have been allowed to use also seven toroidal coils (of inductances between 0.3 and 13 henries) wound on cores made of very fine (No. 38 B. & S.) iron wire. Such cores are, of course, extremely expensive, but the disturbing

effects of eddy currents in them are practically negligible for the purposes of this paper.

THE DEMAGNETIZING OF THE CORE OF A LARGE ELECTROMAGNET.

In order to be able to study satisfactorily the magnetic properties of a given piece of iron or steel, it is usually necessary that one should know with some accuracy the magnetic state of the specimen at the outset, and, especially when the metal has the form of a closed ring or frame, the previous history of which is unknown, the only safe pro-

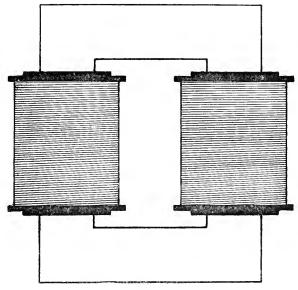


FIGURE 15.

The electromagnet Q, which has a laminated core made of sheet iron one third of a millimeter thick and weighs about 300 kilograms.

cedure is to demagnetize the iron as completely as possible before one makes any experiments upon it. If the metal has the form of a long rod in a solenoid, or of a slender ring wound about uniformly with insulated wire and magnetized in the direction of its circumference, it is easy to send through the coil which surrrounds the iron a long series of currents alternately in opposite directions, which, starting with a value that shall subject the core to a magnetic field at least as strong as any to which it has been previously exposed, gradually de-

crease in intensity to zero. One common way of doing this is to attach the coil to the secondary of a sufficiently powerful alternate current transformer so arranged that the primary coil may be slowly withdrawn to a long distance from the secondary. In the case of the soft iron wire the demagnetization is sometimes accomplished by heating the wire red hot.

It is often a matter of considerable difficulty to remove entirely the effects of previous magnetization from the completely closed massive core of a large transformer: even if the source of a current in the exciting coil has a high voltage, several seconds may be required to established the current, and the use of an alternating demagnetizing current in the coil, with any commercial frequency, is barred out. If a powerful storage battery be connected to the exciting coil through a commutator and a suitable "liquid rheostat," one may begin with a sufficiently strong current  $(I_0)$  and, after reversing this several times



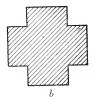


FIGURE 16.

Forms of , the cross-sections of the laminated cores of the electromagnets Q and R.

by hand, increase a little the rheostat resistance so as to decrease the current slightly, then reverse this weaker current a number of times, and thus proceed until the current is reduced to a very small value; but if the core is very large, the operation may take a couple of hours even if the number of steps is not excessive, and after all, it is not easy to tell whether the work has been successful. If the initial current was strong enough, if the stages were sufficiently numerous and properly spaced, and if the number of reversals at each step was great, one may, of course, expect to find the core pretty thoroughly demagnetized, but to test the matter it is usually necessary to undo what has been accomplished by determining the amount of magnetic flux sent through the core when a current of given intensity (I) is sent through the exciting coil. This amount ought to be the same whether this testing current has the same direction as that of the last application of the large current  $(I_0)$  or the opposite direction, and unless one

has a hysteresis diagram for the core obtained by using currents which range exactly between  $+I_0$  and  $-I_0$  the whole work must be done twice. The determination of the flux changes may be made very conveniently with the help of a fluxmeter, but if the highest accuracy is required, it is better to take an oscillogram of the building-up curves of the current when the core starts from its state of supposed neutrality.

If the core of a large electromagnet is not quite closed, it is comparatively easy to demagnetize the iron almost completely and to prove that this has been done; indeed, if the gap has the proper width, the

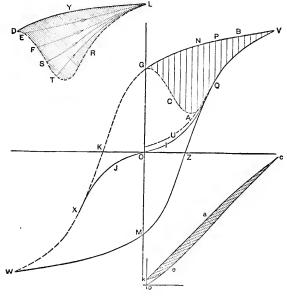
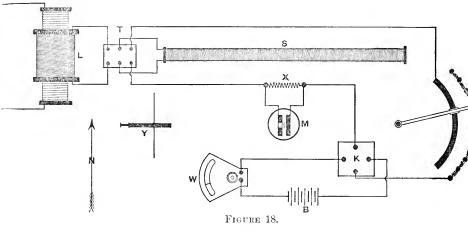


FIGURE 17.

iron practically demagnetizes itself in a wonderful manner. An instance of this was given by Professor Thomas Gray in the case of a 40 K. W. transformer, and I found that the hysteresis diagram for a certain electromagnet which has a solid core the area of which in its slenderest part is more than 450 square centimeters, consists practically of a single straight line when the air gap has a width of 35 millimeters. With this magnet, using an excitation of either 7800 ampere-turns or 15,800 ampere-turns, I obtained current-time curves which were wholly indistinguishable even when much enlarged and

superposed on a screen, whether the current had the same direction as its predecessor or the opposite direction.

If the core of an electromagnet happens to be a straight bar, or a straight bundle of wire, it may be demagnetized by a long series of currents which have alternately one direction and the other, and which slowly decrease in intensity from an initial value which may be considerably smaller than the current which magnetized the iron. Figure 17 shows the results of experiments upon a rod of soft steel 80 diameters long in a long solenoid. The arrangement of the apparatus is shown in Figure 18. The extreme value of the magnetizing field was 27 gausses, and the average moment per cubic centimeter which the



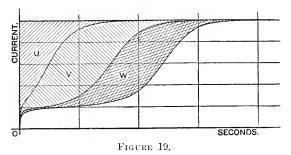
field caused was 246. At the outset the core was thoroughly demagnetized, then a series of steady currents, each a little stronger than the last, was sent through the coil, and the moment of the rod was determined for each direction of the current. This gave the curve WXOQV. Then the hysteresis diagram VGKWMZV was obtained, and after the core had returned to the condition indicated by the point V, the current was somewhat decreased until the core "reached" the point B, and then this current was reversed in direction one hundred times, after which (when the current had the positive direction) the iron had exactly arrived at the point on the curve OIQV beneath B. The core was then brought to V again, the current was decreased,—this time until the core reached the point P,—this current was reversed one hundred times, and it was then found that when it ran in positive

direction the core had arrived at the point Q. This process, repeated for many points on the line GPV, yielded the curve VQACG. If after being at V the core was brought to a point between P and N. and if after it had been many times reversed the current was decreased by short steps with many reversals at each stage, the core traversed the curve U, whereas if the first drop carried the core no farther than P, the procedure led the core to the origin along the curve I. The lowest point of the curve VQAG lies, of course, nearly over the point Z. The shaded diagram in the upper part of the figure shows a similar curve obtained at another time and drawn strictly to scale. If after many reversals of a comparatively small current the core which started at L reached the point F, and if the current was then slowly increased, the core made the journey indicated by the line FL. shaded diagram in the lower part of the figure is a reduction of a curve obtained with a large induction coil the core of which is a compact round bundle of fine wire 7.5 cms. in diameter and about 85 cms. long. The curves oec, cak, cek, in this diagram correspond to OIQV, VPG, VQAG in the larger figure. The retentiveness of a core of these dimensions is, of course, very small.

Even if much time has been spent in demagnetizing a large closed core by sending through the exciting coil currents alternately in one direction and in the other, of intensities gradually decreasing to a very small final value, it frequently happens that after a much larger current has been put for, say, twenty times through the coil alternately in one direction and the other, the hysteresis cycle does not "close," for the change of flux caused by applying the given current in one direction is not equal to the flux change caused by applying the same current in the other. This fact often makes the accurate determination of a hysteresis diagram for such a core a long and trying piece of work. Some toroidal cores I have never succeeded in demagnetizing The demagnetizing apparatus which I have usually employed in the course of the work here described consists first of a storage battery of forty large cells, a set of rheostats made up of metallic and liquid resistances intended for heavy currents, and a commutator run from the main shaft of the laboratory machine shop, and so arranged as to reverse the direction of the current from the cells every ten seconds. Starting with no resistance in the rheostats, resistance was gradually introduced into the circuit until the current had become very small. After this procedure, the secondary circuit of a specially constructed transformer was attached to the exciting coil of the magnet, and from an initial voltage of about 660, at 60 cycles per second, the electromotive force was gradually decreased until the current became too small to measure. In some cases it seemed better to omit the second part of the process.

THE ESTABLISHMENT OF A STEADY CURRENT IN THE COIL OF AN ELECTROMAGNET.

If the circuit of the exciting coil of an electromagnet contains a battery of storage cells of constant voltage E, and if this circuit be suddenly closed, the strength of the current will rise more or less gradually from its initial zero value to E/r amperes, where r is the whole resistance of the circuit in ohms. In the case of a given magnet, with a given electromotive force in the coil circuit, the manner of growth of the current depends very largely, as we have seen, upon the

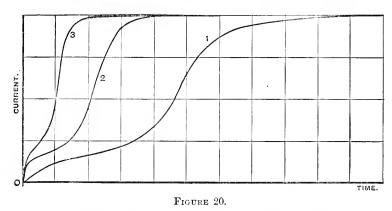


Currents from a battery of 20 storage cells in the circuit of a coil of 2788 turns belonging to the magnet Q. Before the middle curve was taken, the core was carefully demagnetized. The upper and lower curves represent direct and reverse currents, respectively. The areas V and W are equal.

magnetic state of the core when the circuit was closed. The three curves of Figure 19, which are carefully made reproductions of the photographed records of an oscillograph, show the march of the current from a battery of 20 storage cells in the circuit of a coil of 2788 turns belonging to the magnet Q under three different sets of conditions. If after the core had been demagnetized as thoroughly as possible, by the method already described, the circuit was suddenly closed, the current followed the middle curve of the three. If the current was allowed practically to attain its maximum value, and if then a commutator in the circuit was reversed and, at intervals of a few seconds, reversed again and again, and if finally the circuit was broken, it was possible by closing the commutator again in the proper direction, to make the new current follow either the upper or the lower curve of the diagram. If this current coincided in direction with the last current through the

coil, the current was "direct," and its rise was represented by the upper curve. If the new current had a direction opposite to that of the last current through the coil, the current was "reverse," and followed the lower curve. The areas V and W are practically equal.

It is evident that, other things being equal, the rapidity of rise of the current in a circuit which contains a coil wound around the core of an electromagnet will depend very much apon the number of turns in the coil. Figure 20 shows reverse curves from the magnet R. The actual strengths of the currents were 6, 3, and 1.5 amperes respectively, and the numbers of turns in the exciting coils were 85, 170, and 340.



Curves showing the growth of currents in coils of 340 turns, 170 turns, and 85 turns belonging to the magnet R. The same electromotive force was used for all the cases, and the final values of the currents were 6 amperes, 3 amperes, and 1.5 amperes.

The electromotive force was the same in all three cases. The horizontal units are tenths of seconds.

Although the typical current curve for the coil of an electromagnet wound in many turns about the core has two points of inflexion if the core is laminated, both of these disappear if the change of the magnetic flux through the circuit due to the current is small enough, and occasionally one finds an oscillogram which seems to have only one point of inflexion. Some of the direct curves shown in Figures 5, 23, and 28 are everywhere convex upward. Among the nearly three thousand photographed oscillograph records taken for use in this paper no one is concave upward at the very start, but a curve of this kind, with one point of inflexion, has been shown by Dr. Thornton, and I have

many curves which become concave upward very near the origin. In current curves belonging to the coil of an electromagnet which has a large closed, solid core, there are often two points of inflexion, but many of even the reverse curves are everywhere convex upward. Figure 21 shows curves taken for the coil of the large magnet P in the circuit of which was a storage battery of voltage 84. When each current started, the core was nearly neutral.

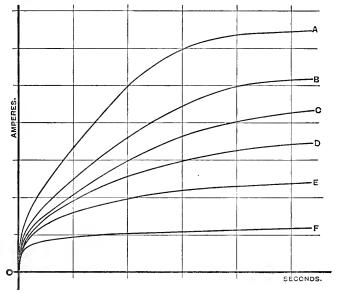


FIGURE 21.

Curves showing the manner of growth of currents of various final strengths in the coil of 2823 turns belonging to the magnet P. The gap was closed and the core was nearly neutral at the beginning of each current. The applied voltage was the same (84) for all the curves.

When the coil of a transformer, the core of which is built up of such thin plates of soft iron as are used in the best practice, is subjected to an alternating electromotive force of extremely high frequency, the disturbing effect of eddy currents in the iron are, of course, very apparent, but the manner of growth of a current under a constant electromotive force is usually not very greatly affected by such currents.

The fact that the susceptibility of the iron is by no means constant, materially alters the shape of a current curve when iron is introduced into a circuit; nevertheless, it is instructive to compare the manner of

growth of a current in the coil of an electromagnet which has such a core, with that of a current in a circuit of fixed inductance, without attempting at the outset to account mathematically for the differences, though it will be easy to do so later on.

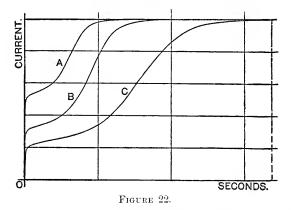
In the case of a simple circuit, without iron, of resistance r ohms and constant inductance, L henries, which contains a constant electromotive force of E volts, the rise of the current I when the circuit is suddenly closed follows the law

$$I = \frac{E}{r} (1 - e^{-\frac{rt}{L}}), \tag{16}$$

and attains the fractional part k of its final value (E/r) in the time

$$t = -\frac{L}{r} \cdot \log_e (1 - k), \tag{17}$$

which is independent of the ultimate current strength and involves only the time constant (L/r) of the circuit. If the circuit is made



Curves which show the manner of growth of currents in a coil of 1394 turns belonging to the magnet Q, to a given final value, when the applied voltages were 82, 41, and 20.5, nearly. In each case the core was neutral at the outset.

up partly of non-inductively wound resistance wire, and partly of helices, r may be kept constant, while L is changed, by changing the relative proportions of the two parts; or r may be altered while L is constant, by increasing or decreasing the non-inductive portion of the circuit.

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If E/r and L are given, different values of E may be used by giving properly corresponding values to the non-inductive resistance, and if the "building-up time" of the current under given initial conditions in the core be defined as the number of seconds required for the current to attain any arbitrarily chosen fractional part of its final value, this time will be inversely proportional to E. In the case of a circuit which has one or more iron cores the phenomenon is much less simple, and if the cores be of solid metal, the effects of eddy currents may complicate the problem seriously; but although under these circumstances the law of proportionality no longer holds, it is almost universally true that the establishment of a current of given final intensity

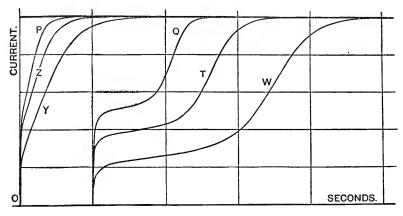


FIGURE 23.

Direct and reverse current curves for the magnet Q with a given final excitation of 2650 ampere turns, under applied voltages of 82, 41, and 20.5, nearly.

in the coil of a given electromagnet can be accelerated by increasing very much the applied electromotive force and then introducing a sufficient amount of non-inductive resistance to make E/r the same as before.

Figure 22 shows current curves for the magnet Q under a fixed final excitation of 2650 ampere-turns. In curves A, B, C, the currents were caused by 40 cells, 20 cells, and 10 cells, respectively, and these currents were made equal by adding to the circuit in each case a suitable non-inductive resistance. Before each of these curves was taken, the core of the magnet was carefully demagnetized by the elaborate process described above. After the magnet Q had been put a good many times through a cycle with a given maximum excitation

of 2650 ampere turns, under one of the voltages just named, direct and reverse curves were taken with the help of the oscillograph. Careful reproductions of these curves are given in Figure 23: to avoid confusion the reverse curves are drawn from a separate time origin.

If in a circuit which contains no iron, E and r be kept constant, while L is changed, the building-up time as defined by equation (17) will be proportional to L. Of course no such simple relation holds when the circuit includes the magnet Q; Figure 24 shows current curves for the same final value of 2.60 amperes, under an applied elec-

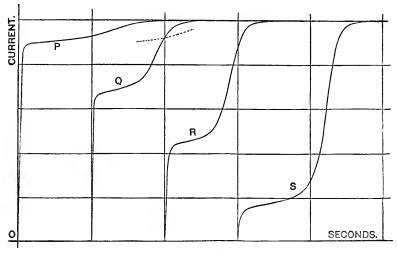


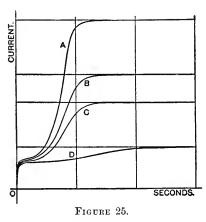
FIGURE 24.

The manner of establishment of a current of final strength 2.60 amperes, in the coil circuit of the magnet Q, under a voltage of 82, when the number of active turns was 407, 823, 1394, or 2788.

tromotive force of about 82 volts, for exciting coils of 407 turns, 823 turns, 1394 turns, and 2788 turns. For convenience, the curves are drawn from different time origins. The dotted line which crosses curve Q calls attention to the fact that if curves P and Q were drawn from the same origin, the former would cross the latter.

If in a circuit without iron E and L were kept constant while r was varied, the building-up time (L/r) would be inversely proportional to the resistance of the circuit, or, since the electromotive force is fixed, directly proportional to the current strength. There is no approximation to this in a circuit which contains iron. The current curves shown in Figure 25 were obtained from the electromagnet Q when

2788 turns were used in the exciting coil and a battery of 40 storage cells with a voltage of about 82 furnished the electromotive force. Curve C evidently corresponds to a case where the total resistance in the circuit is about twice as great as in the case represented by A, but for every value of k the building-up time is greater for C than for A, though the difference becomes very small at the end. A comparison between A and D shows the same fact. Before each of the curves A, B, C, D, was taken the core of the magnet was carefully demagnetized. Figure 26 exhibits current curves taken for different values of r with the same coil of the magnet Q and with the same electromotive force as the curves just mentioned. In each of the cases



Currents in the coil of the electromagnet Q for four different values of r when E and the number of magnetizing turns were fixed. At the starting of each current the core was magnetically neutral.

shown in Figure 26 the core was put several times through a cycle before the direct and reverse oscillograms were taken. The records are reproduced as accurately as possible; B, C, and D run together in a complicated manner, and the same tendency is shown in the reverse curves G, H, I, but in general the longer building-up times belong to the lower currents.

If in an inductive circuit without iron r and L are fixed, the building-up time will be independent of the value of E, but this is not the fact if the circuit contains an electromagnet. Figures 27 and 28 show current curves obtained from the coil of 2788 turns belonging to the magnet Q. In all the curves of each diagram the value of r was the same, but the voltage of the battery in the coil circuit had three differ-

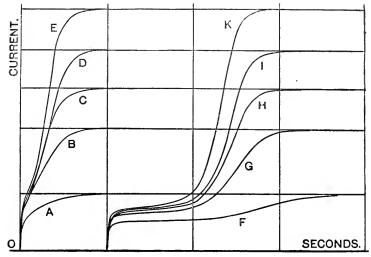
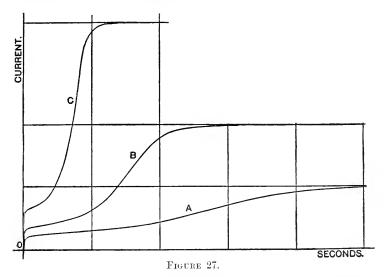


FIGURE 26.

Direct and reverse current curves in the coil of the electromagnet Q for five different values of r when E and the number of active turns were kept fixed.



Currents in the coil of 2788 turns belonging to the magnet Q for three different values of the applied voltage with the same value of r. At the starting of each current the core was magnetically neutral.

ent values the largest of which (belonging to the curves C, M, N) was about 82: in this case the current was almost exactly 2.50 amperes. Before each of the curves A, B, C was taken the core was thoroughly

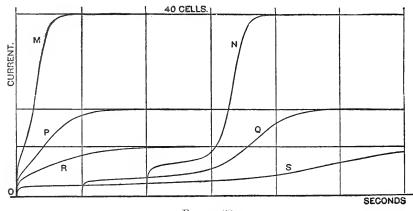


Figure 28.

Direct and reverse currents in a coil of 2788 turns belonging to the magnet Q for three different values of the applied voltage, but the same value of r.

demagnetized: R, P, M are direct curves, but S, Q, N are reverse curves. It is evident that the building-up times are not even approximately independent of E.

Figure 29 shows the records of an oscillograph in a secondary circuit in which were a few turns of wire wound around the core of the magnet Q. The primary circuit contained, besides the storage battery, a rheostat and an exciting coil of 1394 turns. When the primary circuit

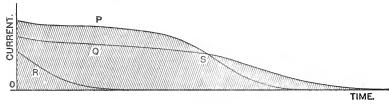


FIGURE 29.

was suddenly closed with such a resistance in the rheostat that the final strength of the current was 1.1 amperes, the induced current had the value indicated by the curve Q; when the rheostat resistance was suddenly removed so as to bring the final strength of the current up to

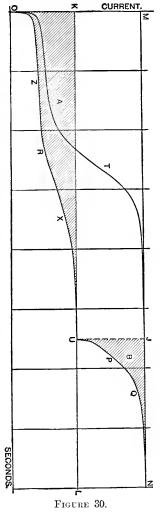
2.3 amperes, the induced current curve was R. The sum of the areas under the curves Q and R was 74.3 square centimeters. The curve P

shows the current record in the secondary circuit when the primary circuit was suddenly closed with no resistance in the rheostat: the area under this oscillogram was 74.6 square centimeters. All the currents were reverse currents. Most of the area determinations of this paper were made with a Coradi "Grand planimètre roulant et à sphère."

Figure 30 shows a careful reproduction of the record of an oscillograph in the primary circuit of the arrangement just described. These curves were taken on the same day as those of the last figure. In this case the flux change due to the current which gave the curve T was to the sum of the flux changes caused by the partial currents as 1130 to 1126. These numbers do not show any real difference between the corresponding physical quantities, but point to difficulties of measurement.

THE EFFECT OF THE MAGNETIC CHARAC-TERISTICS OF THE CORE UPON THE MAN-NER OF GROWTH OF A CURRENT IN THE COIL OF A LARGE ELECTROMAGNET.

If under the application of a constant electromotive force to the coil circuit of an electromagnet a current grows gradually in the coil to its full value, the magnetic flux in the core at any moment depends, as we have seen, not only upon the instantaneous strength of the current, but also upon the magnetic state of the core at the beginning. Moreover, if the core is solid, it is clear that the magne-



tizing field to which the interior of the iron mass is exposed may be quite different at any instant from what it would be if eddy currents were nonexistent. If, however, the core is built up of such thin sheets

of iron as are used in good transformers, a fair approximation to the form which the current curve will have under any given circumstances can be made if one has an accurate statical hysteresis diagram of the core for the range required, and if the core is made of very fine varnished wire, as in the case of loading coils for long telephone circuits, a hysteresis diagram obtained either from a long "step-by-step series" of measurements or from one or more oscillograms, enables one to predict with accuracy what the form of a current curve will be for any practical case. These last statements are based on experiments such as those recorded below.

As a result of a long series of measurements, it appears that when the core of the magnet Q has been well demagnetized and a series of steady currents each a little stronger than the preceding one are established in the exciting coil, the magnetic flux through the core in thousands of maxwells follows fairly accurately the course indicated in the following table:

TABLE I.

| Magnetic Flux. | Ampere Turns.                                         | Magnetic Flux.                                                                                             |
|----------------|-------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| 35             | 1100                                                  | 1208                                                                                                       |
| 146            | 1200                                                  | 1238                                                                                                       |
| 386            | 1300                                                  | 1262                                                                                                       |
| 622            | 1400                                                  | 1285                                                                                                       |
| 787            | 1500                                                  | 1309                                                                                                       |
| 929            | 1600                                                  | 1331                                                                                                       |
| 1013           | 1700                                                  | 1352                                                                                                       |
| 1086           | 1800                                                  | 1369                                                                                                       |
| 1137           | 1900                                                  | 1390                                                                                                       |
| 1176           | 2000                                                  | 1409                                                                                                       |
|                | 35<br>146<br>386<br>622<br>787<br>929<br>1013<br>1086 | 35 1100<br>146 1200<br>386 1300<br>622 1400<br>787 1500<br>929 1600<br>1013 1700<br>1086 1800<br>1137 1900 |

Figure 31 reproduces the table graphically in the full curve: the vertical unit is a thousand maxwells, and the horizontal unit is 139.4 ampere-turns, to suit the case when the particular exciting coil used has 1394 turns. The ordinates of the dotted curve represent twice the corresponding values of the slope  $(\lambda)$  of the other. A template of the curve B was made as accurately as possible from a large piece of sheet

zinc; this was fastened down on a table over a number of sheets of coordinate paper, and the value of  $\lambda$  was determined by measuring on the paper the position of a straight edge which touched the template at any desired point.

| Current in Amperes. | Log [(13.94)λ]. | Current in Amperes. | Log [(13.94)λ]. |
|---------------------|-----------------|---------------------|-----------------|
| 0.00                | 0.445           | 0.55                | 1.135           |
| 0.05                | 0.860           | 0.60                | 1.025           |
| 0.10                | 1.248           | 0.65                | 0.943           |
| 0.15                | 1.602           | 0.70                | 0.860           |
| 0.20                | 1.715           | 0.75                | 0.797           |
| 0.25                | 1.672           | 0.80                | 0.746           |
| 0.30                | 1.594           | 0.90                | 0.700           |
| 0.35                | 1.496           | 1.00                | 0.635           |
| 0.40                | 1.399           | 1.10                | 0.621           |
| 0.45                | 1.312           | 1.25                | 0.606           |
| 0.50                | 1.209           | 1.30                | 0.591           |

If after the core of Q had been demagnetized, a steady electromotive force of E volts were applied to the exciting circuit of resistance r ohms, containing the coil of 1394 turns, and if eddy currents were nonexistent so that the core followed the statical magnetizing curve, the march of the current (in amperes) would be given by the equation

$$E - ri = 13.94 \,\lambda \cdot \frac{di}{dt}, \tag{18}$$

$$t = \int_0^i \frac{13.94 \,\lambda}{E - ri} \,di. \tag{19}$$

If from an actual current curve obtained from Q for a given journey of the core we were to determine the corresponding magnetizing curve for the metal (flux versus coil current), we should find that the values of the flux, for small values of the current, at least, would fall short of the flux values which the same currents would cause if they were to act

for some time because the magnetizing field is less than that due to the coil current by that due to the eddy currents. If, therefore, from the numbers of Tables I and II we were to determine the form of a current curve for Q, corresponding to any journey of the core, this would fall somewhat below the actual curve at the beginning. The core of Q has, however, a typical magnetizing diagram, and the theoretical curves are instructive as showing what the actual curves would be if the same core were more finely divided. The effect of eddy currents can be seen in the curves for this magnet given above.

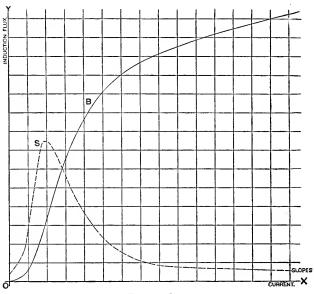


FIGURE 31.

Magnetization curve for the core of the magnet Q which at the outset is in a neutral state. The ordinates of the dotted curve represent twice the slopes of the other curve.

The boundary of the shaded area in Figure 32 shows twice the value of the integrand

$$w = \frac{13.94 \,\lambda}{E - ri} \tag{20}$$

for the case E=26, r=20: the horizontal unit is one tenth of an ampere. The vertical line corresponding to i=1.3 is evidently an asymptote. The area under the curve from the beginning to the ordi-

nate representing any given value of the current shows, in twentieths of a second, the time required, under the given conditions, after the circuit is closed for the current to attain this value. It is easy to determine a series of such areas with the help of a good planimeter, and the full curve of Figure 32 actually represents the growth of the current in the case mentioned according to my measurements of the large diagram of which Fig. 32 is a very much reduced copy: for this curve the horizontal unit is one tenth of a second and the vertical unit is one fifth of an ampere. This curve has the general form of most of the

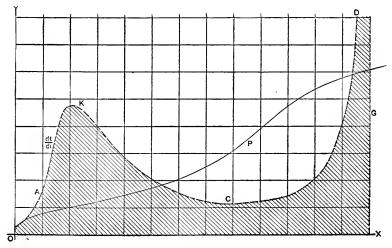


FIGURE 32.

The ordinates of the boundary of the shaded area represent  $2\left(dt/di\right)$  for  $E=26,\ r=20.$  P shows the theoretical form of the corresponding current curve.

current curves which one obtains with a transformer the core of which is at the outset neutral, but it is evident that in any case where the final value of the current is small enough the asymptote will be moved so far to the left that the integrand curve will rise continually from the beginning, without the maximum and minimum values, and the current curve will have the everywhere convex shape that we find in practice when we cause the current to grow by short steps in the manner indicated by the curve U in Figure 4.

Figure 33 shows building-up current curves (A, b, c) for E = 26, and r = 20, 40, and 60, respectively. The dotted curves B and C are copies of b and c with ordinates so magnified that the curves have the

same asymptote as A. According to this diagram the current attains 75 per cent of its own final value more quickly when r is 40 than when r is 20, but B crosses A at the point x and the current seems to reach practically its full strength sooner in the latter case. The curve C first crosses the curve A and then B. It would be easy to show from a series of oscillograph records for similar cases that the characteristics of the theoretical curves correspond in general to fact.

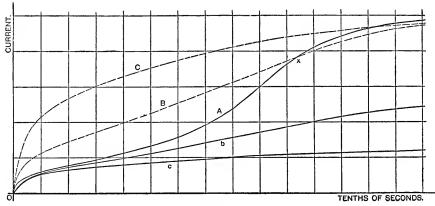


FIGURE 33.

Forms of current curves for Q deduced from theoretical considerations. The coil has 1394 turns and contains a storage battery of voltage 26. C is everywhere convex upward: A and B have two points of inflexion.

If with the core of the magnet Q initially neutral a steady current of given strength be established in the coil of 1394 turns, by use of a storage battery of voltage E, the integrand will be for every value of the current inversely proportional to E (since E/r is given), and the building-up time will be inversely proportional to the applied electromotive force, as it would be if the inductance were fixed. For a given exciting coil, the general shape of the curve for a given current is independent of the applied voltage. Curves A, C, and D of Figure 34 are the current curves computed for E=26, 52, 104, and r=20, 40, and 80: the maximum value of the current is the same in every case. G and F are the current curves computed for E=26, r=80, and for E=104, r=320.

As has been explained already, it is difficult to obtain an accurate hysteresis diagram for a very large core by the ordinary ballistic methods with such galvanometers as are usually to be found in the

testing room, but it is fairly easy to attach extra weights to the suspended system (Figure 35) of a good d'Arsonval or Thomson Mirror galvanometer which shall so increase the moment of inertia that the time of swing shall be lengthened to five or ten or twenty minutes. With an instrument thus modified it is usually possible, by changing the intensity of the current in the exciting coil by small steps, to deal satisfactorily with very large masses of iron. It is of course desirable to use a rather high electromotive force in the exciting coil in order

TABLE III.

| Ampere Turns. | Flux in Thousands of Maxwells. | Ampere Turns. | Flux in Thousands of Maxwells. |
|---------------|--------------------------------|---------------|--------------------------------|
| 1812          | 1371                           | -131          | 772                            |
| 1394          | 1351                           | -148          | 73 <del>4</del>                |
| 1255          | 1340                           | -181          | 552                            |
| 1031          | 1316                           | -234          | 332                            |
| 809           | 1285                           | -294          | 22                             |
| 474           | 1211                           | -392          | -465                           |
| 392           | 1186                           | -474          | -661                           |
| 294           | 1148                           | -809          | -1010                          |
| 234           | 1121                           | -1031         | -1128                          |
| 181           | 1099                           | -1255         | -1214                          |
| 148           | 1070                           | -1394         | -1265                          |
| 131           | 1060                           | -1812         | -1371                          |
| 000           | 953                            |               |                                |

to make the building-up time short, and to reduce the current to the desired strength by introducing extra non-inductively wound resistance into the external circuit. In order to test this matter thoroughly, I measured with great care, by aid of a modified Rubens-du Bois "Panzer Galvanometer," the flux changes in the core of the magnet Q (the area of the cross-section of which is more than 150 square centimeters), corresponding to a hysteresis cycle for an excitation of 1812 ampere turns. I then determined the same total flux change by means of planimeter measurements of the areas under a long series of

oscillograph records; all the testing instruments were different in the two cases, and no comparison was possible until the final results were

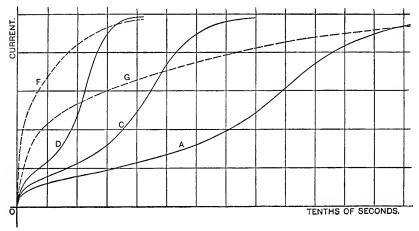


FIGURE 34.

Theoretical forms of current curves in a coil of 1394 turns belonging to the magnet Q. In practice these would be somewhat modified by eddy currents.

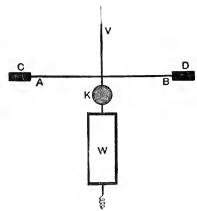
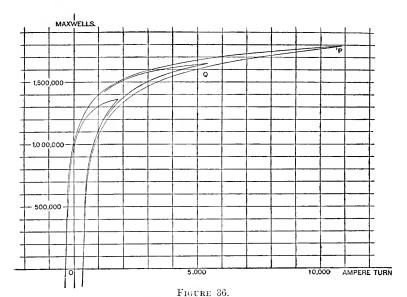


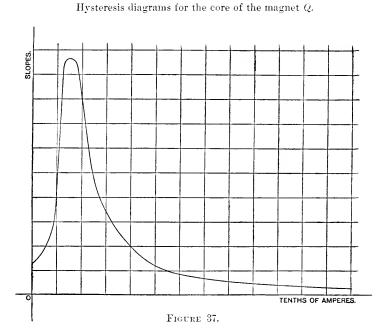
FIGURE 35.

The horizontal rod AB is threaded and the brass masses C,D can be screwed on the rod as far as is necessary. The system must be accurately balanced.

obtained and were found to differ from each other by only one part in about fourteen hundred. The labor of reducing the oscillograms was very great, and this extremely close agreement must be considered accidental, since it is not easy to make a large mass of iron go over exactly the same magnetic journey twice.

Hysteresis diagrams for the magnet Q and corresponding to maximum excitations of 1812, 5370, and 10,880 ampere turns are given in Figure 36. Some results of measurements of the flux changes in the core for the first of these cycles are given in Table III





After a curve had been drawn on a very large scale to represent the numbers of Table III, a zinc template was made from it, by aid of which and a long "straight-edge" the slopes of the curve could be determined with some accuracy. The next diagram (Figure 37) shows the slope as a function of the strength of the current.

When the slope for any point of the curve is multiplied by (13.94) / (E-ri), where E and r are given, the result is the value of dt/di for the reverse current curve when the applied voltage is E and the resistance r, for the given value of i. Figure 38 exhibits dt/di for E=19.5, and r=15.

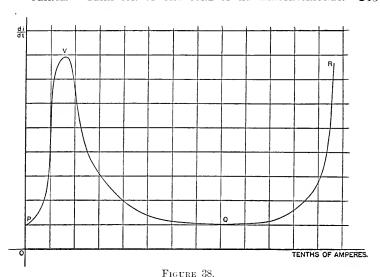
The actual curve was drawn on a large scale, and the area X from x=0 to x=i, for a number of different values of i were measured by a planimeter in terms of the unit square of the figure; this area expressed in tenths of seconds the time required for the reverse current to attain the strength i. A few values of X are shown in the next table.

| i.   | X/10.        | i.   | X/10. |
|------|--------------|------|-------|
| 0.05 | 0 057        | 0.50 | 1.750 |
| 0.10 | 0.155        | 0.60 | 1.875 |
| 0.15 | <b>0.494</b> | 0.70 | 1.985 |
| 0.20 | 0.878        | 0.80 | 2.088 |
| 0.25 | 1.141        | 0.90 | 2.188 |
| 0.30 | 1.325        | 1.00 | 2.294 |
| 0.35 | 1.471        | 1.10 | 2.412 |
| 0.40 | 1.579        | 1.20 | 2.632 |
| 0.40 | 1.579        | 1.20 | 2.632 |

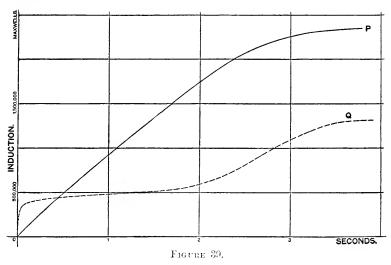
TABLE IV.

Every form of current curve which I have met in practice can be closely imitated by a theoretical curve; but all these curves have at the outset a direction differing widely from the horizontal. Dr. Thornton, however, shows a beautiful curve which at the beginning is convex downward and has at the start a direction not very different from that of the axis of abscissas.

Before one uses an oscillograph for purposes of accurate measurement, one must make sure that the instrument has been properly set up. When the drum which carries the sensitive film or paper is at

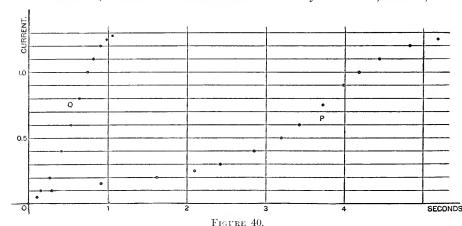


The value of dt/di for a reverse current in a coil of the magnet Q when E=19.5 and r=15.



The full curve shows the rate of increase of the flux of magnetic induction through the core of the magnet Q while a reverse current of 1.3 amperes is being established in the exciting coil of 1394 turns. The current curve is shown on an arbitrary scale by the dotted line.

rest, a current sent through the conductor should give a perfectly straight record accurately perpendicular to the base line, and the length of this record should be proportional to the strength of the current. It sometimes happens that an oscillograph which records accurately the march of a moderate current lags in its indications a very little behind the strength of a comparatively feeble current owing to the viscosity of the oil used for damping, which only then becomes troublesome. I have myself had sad experience in drawing from the records of an instrument of this sort, which I thought I had carefully calibrated, elaborate inferences which were contrary to fact. If, however,



Theoretical forms of direct and reverse current curves for a coil of 1394 turns belonging to the magnet Q when the resistance of the circuit is 8 ohms and the applied voltage is 10.4.

one has at hand, first, a well-constructed and mounted ballistic galvanometer with a period of from eight to ten minutes, and means of damping the swings of the suspended system (electromagnetically or otherwise) without touching it, and secondly, some kind of chronograph designed to close and after a given interval to open again any circuit to which it may be attached, it is easy to test almost any supposed fact about the growth of the flux through the core of an electromagnet.

The toroids I used had cores made of extremely fine, varnished iron wire, costing about four dollars per kilogram. For some of these I determined by ballistic methods, as carefully as I well could, the hysteresis diagrams for several excitations, and then compared with these other diagrams obtained from the oscillograph records of current curves for

the same magnetic journeys of the cores, but I could not detect any differences which did not lie far within the small uncertainty which the viscosity of the oil in the oscillograph may be supposed to cause. It does not seem worth while to print a long series of numbers to illustrate this kind of comparison though the labor was great.

If, then, the core of an electromagnet is made of iron wire not more than one tenth of a millimeter in diameter and carefully varnished, it seems to be true within the limits of accuracy of my measurements and for the comparatively moderate excitations used, that if the core

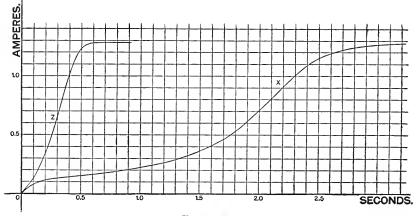
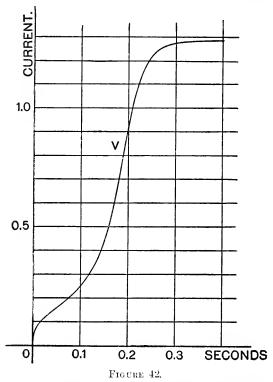


FIGURE 41.

Theoretical forms of direct and reverse current curves for a coil of 1394 turns belonging to the magnet Q when the resistance of the circuit is 15 ohms and the applied voltage is 19.5.

is in a given magnetic state at the start, the change of the flux of magnetic induction caused by a current which grows from zero without decreasing to a given final intensity, is quite independent of the manner of growth of this current. It may grow continuously or by steps, and if eddy currents are not appreciable, the condition of the core at the end is the same. According to this, one would get exactly the same hysteresis diagram from an accurately drawn current curve of the form V (Figure 4) corresponding to any change of current in the exciting coil as from the corresponding U diagram or from any slow step-by-step ballistic method. Nothing of the nature of time lag, if it exists at all, affects the growth of the induction in the iron appreciably. Even in the case of an ordinary transformer, where the effects

of eddy currents are very noticeable at the early portions of most current curves, the whole change of flux due to a given current in the coil is the same apparently whether the current grows steadily or by steps; in this case an accurate diagram of the U form and a step-by-step ballistic method with a proper galvanometer may be expected to yield



Theoretical form of reverse current curve for a coil of 1394 turns belonging to the magnet Q, under an electromotive force of 208 volts. The resistance of the circuit is 160 ohms.

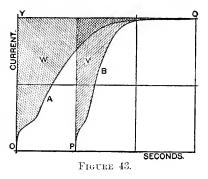
identical results within the limits of the measurements. This statement seems to be justified by such comparisons of the two as that recorded on page 142, which required many days in the making. From a current curve we may expect to get a hysteresis diagram good enough for any commercial purpose, but differing slightly at the beginning from the statical diagram found ballistically. Of course, it would not be easy to get any very accurate information, as some of the curves

given in this paper show clearly, from a current curve taken in the exciting coil of a magnet which has a large solid core.

It will be evident from what precedes that it is possible to predict accurately the building-up curve of a current in the coil of an electro-

magnet with fine wire core, from a corresponding hysteresis diagram obtained by aid of a ballistic galvanometer of long period, and one of the old methods of procedure.

Figure 43 shows two reverse current curves for a toroidal magnet of about one third of a henry inductance belonging to the American Telephone and Telegraph Company. The final strength of the current was the



same (1.42 amperes) in both cases, but the applied electromotive force was 10.9 for the left-hand curve and 21.5 for the other. The disturbing effects of eddy currents were here (as will be shown in the sequel) wholly inappreciable. We should be justified in expecting that each of these current curves would yield by aid of a good planimeter a hysteresis diagram substantially the same as any ballistic step-by-step method would furnish for the same magnetic journey of the core.

The Influence of Eddy Currents upon the Apparent Magnetic Behavior of the Core of a Large Electromagnet in the Coil of which a Current is growing.

If after the solid core of a large electromagnet had been demagnetized we were to establish a steady current in the exciting coil by applying to its circuit a constant electromotive force, eddy currents would, of course, be set up in the core, and at any instant during the growth of the current in the coil the iron at the centre of the core would be subjected to a magnetic field weaker than the field belonging to a steady current of intensity equal to the instantaneous strength of the coil current. If, therefore, we were to attempt to determine the magnetic properties of the core from the record of an oscillograph in the coil circuit, we should find that the induction through the core corresponding to a given instantaneous current intensity in the coil was less than the flux belonging to a steady current of the same intensity as deter-

mined from a statical hysteresis diagram. The same phenomenon appears when an electromagnet with finely laminated core has a secondary coil. The closing on itself of a secondary coil wound on the core of an electromagnet when a current is being established in the primary will, therefore, expedite at first the rise of this current, but the area over the current curves ought to be the same in the two cases, and we must expect, therefore, the building-up time to be somewhat longer when the secondary coil is closed than when its circuit is broken.

It is to be expected, of course, that the curves which show the march of the current in the primary circuit will be noticeably different in form when the secondary circuit is closed and when it is open; for this is often the fact in the case of two neighboring circuits which have fixed self and mutual inductances  $(L_1, L_2, M)$  if one of them containing an electromotive force E be suddenly closed at the time t = 0, while the other, which contains no electromotive force, is closed. Here

$$L_1 \cdot \frac{dI_1}{dt} + M \cdot \frac{dI_2}{dt} + r_1 \cdot I_1 = E_1,$$

$$M \cdot \frac{dI_1}{dt} + L_2 \cdot \frac{dI_2}{dt} + r_2 \cdot I_2 = 0,$$
(21)

where  $r_1$ ,  $r_2$  are the resistances of the circuits and  $I_1$ ,  $I_2$  the currents in them.

If 
$$\lambda = -\frac{(Q-R)}{2S}$$
, and  $\mu = -\frac{(Q+R)}{2S}$ ,

where  $S = L_1 \cdot L_2 - M^2$ ,  $Q = r_2 \cdot L_1 + r_1 \cdot L_2$ ,  $R^2 = Q^2 - 4r_1 \cdot r_2 \cdot S$ ;

$$I_{1} = \frac{E_{1}}{R \cdot r_{1}} \left[ R - \frac{1}{2} e^{\lambda t} (r_{2} \cdot L_{1} - r_{1} \cdot L_{2} + R) + \frac{1}{2} e^{\mu t} (r_{2} \cdot L_{1} - r_{1} \cdot L_{2} - R) \right], \quad (22)$$

$$I_{2} = \frac{E_{1} \cdot M}{R} [e^{\mu t} - e^{\lambda t}], \tag{23}$$

$$\int_{0}^{\infty} \stackrel{\epsilon}{I_{2}} \cdot dt = -\frac{E_{1} \cdot M}{r_{1} \cdot r_{2}}, \text{ and } \int_{0}^{\infty} \left(\frac{E_{1}}{r_{1}} - I_{1}\right) dt = \frac{L_{1} \cdot E_{1}}{r_{1}^{2}}.$$
 (24)

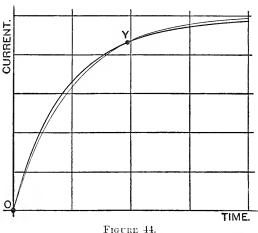
Figure 44 illustrates a typical case where S is positive: the heavy line shows the current in the primary circuit when  $r_1 = 3$  ohms,  $r_2 = 2$  ohms,  $L_1 = 3$  henries,  $L_2 = 2$  henries,  $M = \sqrt{6/3}$  henries,  $E_1 = 12$  volts, when the secondary is closed; the lighter curve shows the rise of the current in the same circuit when the secondary circuit is open.

$$I_1 = 4 \left( 1 - \frac{1}{2} e^{-\frac{3t}{4}} - \frac{1}{2} e^{-\frac{3t}{2}} \right), \tag{25}$$

and 
$$I_1 = 4 (1 - e^{-t}).$$
 (26)

The slope of the first curve is at the outset somewhat greater than that of the secondary curve, but eventually becomes less, the curves intersecting at a point Y. The area between the curve and the asymptote drawn parallel to the axis of abscissas is the same for both cases.

If the circuits just described had in common a large closed iron core, the current curves for open and closed secondary circuit would be



Currents in the primary circuit of an induction coil with air core, when the . secondary circuit is closed (full curve) and when the secondary is open.

much less like each other than the curves of Figure 44 are, even if the core were not solid. We may illustrate this fact by some oscillograms from a transformer which has a laminated core.

Figure 45 shows two typical reverse current curves for the exciting coil of the magnet Q which has 2788 turns, when the circuit of a secondary coil of 1095 turns is (D) open and (C) closed. Both curves rise very rapidly at the start, and then bend suddenly, so as to become almost horizontal for a time, but in the first fifth of a second the curve taken when the secondary is closed attains 40 per cent of its final value, and the other curve only 18 per cent; yet the second curve reaches half its height about two fifths of a second sooner than the first does; and when the secondary is open the current in the primary

circuit reaches 98 per cent of its maximum strength in about \$\frac{2}{6}\$ths of a second less time than when the secondary is closed. In this case the final current was 2.80 amperes. Of course the degree of divergence of the current curve for the primary circuit when the secondary is closed, from the corresponding curve when the secondary is open, depends very much upon the number of turns of the secondary and upon its resistance.

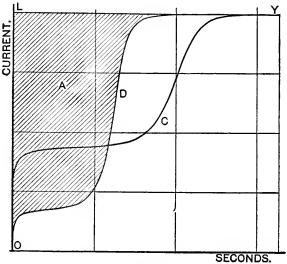


FIGURE 45.

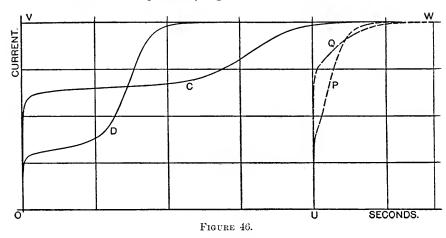
Reverse current curves for the coil of 2788 turns belonging to the magnet Q, when the circuit of a secondary coil of 1095 turns was closed (C) and open (D). The resistance of the primary circuit, which contained a battery of 40 storage cells, was 30 ohms.

Figure 46 shows both reverse and direct curves for the magnet Q when the primary and secondary coils were geometrically alike and each had 1394 turns. The resistance of the primary circuit was about 16.7 ohms.

The curves of Figure 47 belong to a primary coil of 823 turns of the magnet Q. The lines which have O as origin represent currents of about 2.05 amperes due to a storage battery of 10 cells; the lines which start at X were caused by currents of 7.55 amperes from a battery of 40 cells.

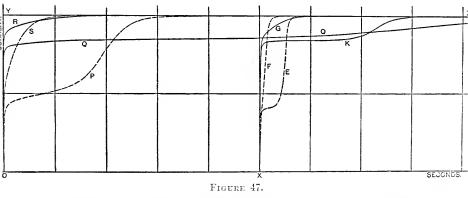
Figure 48 shows direct and reverse curves for a current of 3.30 amperes (due to a storage battery of 40 cells) in a coil of 1394 turns

belonging to Q. The curves M, N were taken with a secondary coil of 16 turns and comparatively high resistance closed; the boundaries



Direct and reverse current curves for a coil of 1394 turns belonging to the magnet Q when a secondary circuit of 1394 turns was closed and open.

of the shaded areas m, n show the forms of the currents induced in this secondary as obtained from an oscillograph in the circuit. Since



Direct and reverse curves representing currents in a primary coil of \$23 turns belonging to the magnet Q, for open and closed secondary circuit. The secondary coil had 2788 turns. For the curves which start at  $\theta$  the voltage was about 20.6; for the curves which begin at X the voltage was about 82 and the maximum current 7.55 amperes.

the number of turns in this secondary was so small and the resistance large, the forms of the curves M, N are not very different from what they would have been if the secondary circuit had been open. The curves V, W were taken with another secondary circuit of 1095 turns closed on itself: the boundary of the area v shows on an arbitrary scale the form of the induced current in this last mentioned secondary circuit.

It is not to be expected, of course, that a current curve for the exciting coil of an electromagnet which has a large solid core will be so much altered in general appearance by the closing of a secondary coil

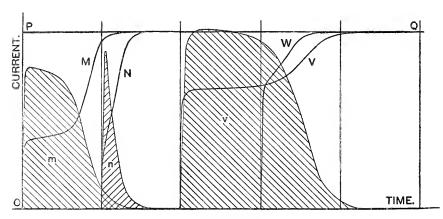


FIGURE 48.

as it would be if the core were divided so as to prevent in large measure the effects of powerful eddy currents which are present when the iron is in one piece.

Even in the case of an electromagnet the core of which is built up of broad varnished pieces of sheet iron, eddy currents in this iron may radically change the form of a current curve unless the sheets are very thin. Figure 49 illustrates this fact by an actual example drawn to scale.

Figure 50 shows curves belonging to a certain transformer. M is a piece of a statical hysteresis curve; N is a similar curve obtained from a reverse current oscillogram. Although the core of this magnet is made up of varnished pieces of sheet iron, the effects of eddy currents, as will be shown more clearly in the sequel, are here very noticeable.

Some instances of the phenomenon just mentioned suggest a possible

pure time-lag <sup>12</sup> of magnetization, like that observed by Ewing and Lord Rayleigh, large enough in the case of a very large core to affect somewhat the forms of the current curves; in fact, I have spent a very long time and have made many measurements upon a great number of oscillograph records in order to see whether any such lag could be shown; but after all allowances have been made for the effects of eddy currents, nothing tangible, if anything at all, remains, for such moderate excitations as I have used with closed, finely divided cores.

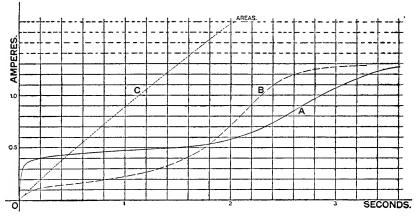


FIGURE 49.

The full line represents the actual form of a reverse current curve in the coil of a certain transformer the core of which is laminated; the curve sketched out by dashes represents the theoretical form as obtained from the statical hysteresis diagram. The dotted curve represents on an arbitrary scale the areas between the real curve and the asymptote; the flux change being nearly proportional to the time.

If to a circuit — without iron and unaffected by any neighboring currents — which has a fixed inductance L, and resistance r, be applied a fixed electromotive force, E, the current-time curve will follow the equation

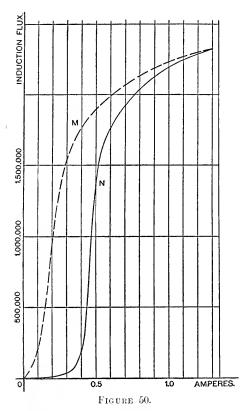
$$I = \frac{E}{r}(1 - e^{-\frac{rt}{L}}),$$

and the current will attain the intensity  $I_0 = E/(r+h)$  at the time  $t_0$  such that

<sup>&</sup>lt;sup>12</sup> G. Wiedemann, Galvanismus, **3**, 738. Ewing, Magnetic Induction, § 84. Gumlich und Schmidt, Electrotechnische Zeitschrift, **21**, 1900. Rücker, Inaugural Dissertation, Halle-Wittenberg, 1905.

$$e^{-\frac{rt_0}{L}} = \frac{h}{r+h}.$$

If, however, the resistance of the circuit at the outset had been (r + h) and if after the final value of the current  $I_0$  for this resistance



M is a portion of a statical hysteresis diagram for a certain transformer under an excitation of 1812 ampere turns. N is a similar curve obtained from a reverse current oscillogram.

had been established, the extra resistance had been suddenly removed from the circuit, the current curve from that instant on would have followed the equation

$$I = I_0 e^{-\frac{rt'}{L}} + \frac{E}{r} (1 - e^{-\frac{rt'}{L}}),$$
or, since
$$I_0 = \frac{E}{r} (1 - e^{-\frac{rt_0}{L}}),$$

$$I = \frac{E}{r} (1 - e^{-\frac{r(t'+t_0)}{L}}).$$

It is clear, therefore, that in the case of a circuit of this kind the last (upper) portion of a step curve of the form U (Figure 4) will have exactly the same shape as the corresponding part of the V curve, although the lower portions may be very different.

If in the case also of a circuit which has one or more finely divided iron cores the flux of induction through the circuit can be considered as a single valued (given) function of the current strength when the

magnetic state of the iron at the outset is given, the upper portion of a curve of the U type (Figure 4) belonging to the circuit will be identical with the corresponding part of a curve of the V type. We need consider only a U curve with one intermediate step. If the induction (N)

through the circuit corresponding to a current of intensity I is  $\phi$  (I), and if the resistance of the circuit is R, the differential equation which determines the growth of the current is

$$E - \frac{dN}{dt} = RI$$
 or  $\frac{\phi'(I) \cdot dI}{E - RI} = dt$ .

Since  $\phi$  is known, the coefficient of dI is known after values have been assigned to the constants E and R. If with a given E, R has the value r, the curve obtained by plotting the coefficient of dI against I will have a shape something like that of the line KCDP of Figure 51, which has the line I = E/r for an asymptote. If with the same value of the electromotive force R has the value (r + h), the curve will have a shape something like that of the line KBDA, which has the vertical

asymptote I = E/(r+h) which passes through Q. If with the core in the state for which the diagram is drawn, the circuit be closed at the time t=0, and if the resistance be (r+h), the time required for the current to attain any value I' less than E/(r+h) is proportional to the shaded area under the curve KBDA from the ordinate axis up to the vertical line x=I'. If, however, the

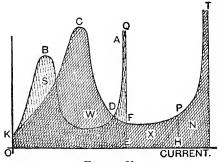
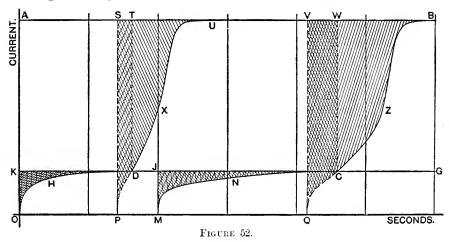


FIGURE 51.

resistance of the circuit had been r, the time required for the current to grow to the intensity I' would be represented on the same scale by the area under the curve KCDP from x = 0, to x = I'. If the circuit were closed when its resistance was (r + h), and if the current were allowed practically to reach its final value for this resistance, as represented by the line OE, and if then the resistance h were suddenly shunted out, the current would grow to its new final value at a rate determined by the fact that the time required to reach the current OH must be equal, on the scale of the diagram, to the area EFPH. If the circuit had been closed first when its resistance was r, the time required for the current to grow from the intensity OE to the intensity OH would still be equal, on the scale used, to the area EFPH, and the shape of the current curve, from E/(r + h) on, would be the same as before. Of course the N of this theory need not be the same as the N of the statical hysteresis diagram for the given magnet; it might

have for any value of I a value which in the case of the statical curve belonged to a current weaker by any given constant or otherwise determined amount. The curve FP must, however, have the same form for a continuously growing current and for one which suddenly begins to increase from the value OE.

As a matter of fact, experiment seems to show that if the core of an electromagnet is made of varnished wire so fine that eddy currents are practically shut out, the upper portion of a U curve with a single intermediate step is exactly like the corresponding portion of the V curve. Figure 52 represents a set of current curves obtained from a number



Current curves for a coil with fine wire core. The second part of a two-stage current is exactly the same as if the current were allowed to grow at once to its final value.

of toroidal coils (with very fine wire cores) connected up in series; the current came from a storage battery of ten cells. When the circuit had its normal resistance, the final value of the current was represented by OA; it was possible, however, to close the circuit with such an extra amount of resistance that the final value of the current should be representable on the same scale as before, by the line OK. The extra resistance could then be suddenly shunted out of the circuit by closing a switch at any time after the lower current had practically attained its maximum strength. When the core had been previously demagnetized, a diagram of this kind had the form  $OHDA^*U$ ; but if the circuit had from first to last its normal resistance, the current curve had a shape accurately represented — when the starting point was shifted to the proper

point (P) on the time axis — by PDXU. The upper part of the curve was in no way distinguishable from the corresponding portion of the U diagram. Mr. John Coulson and I have taken many records of this kind and have not been able to detect any difference between the upper parts of the different kinds of curves. The second part of the U diagram starts off at exactly the same angle with the horizontal that the other curve has when the line KG is crossed. The area OKDHO when divided by the length OK should be the same as the area PSTDP divided by the length OA.

If eddy currents are present, the upper portions of a U diagram and of a V diagram do not entirely agree. Figure 53 represents diagrams

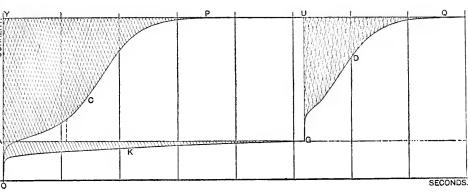


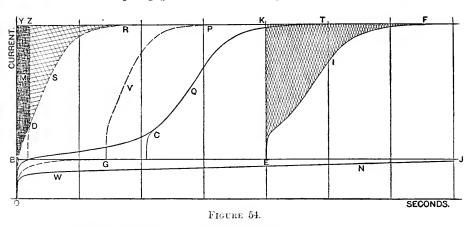
FIGURE 53.

Growth from an originally neutral core of a current in a transformer with a laminated core. The effects of eddy currents are here noticeable.

for the magnet Q which has a laminated core, although eddy currents are not entirely shut out. If the upper part of the U diagram (GDQ) be shifted to the left, it will be found to agree with the curve PCO from P to C, but beyond C the two are quite different, as the dotted line indicates. When the V current, the growth of which is represented by the line OCP, has reached the strength OA, the induction flux through the core is only a small fraction of the flux when a steady current of final strength OA is established in the coil in the manner represented by OKG. The existence of eddy currents is indicated clearly by the fact that the first portion of the curve GDQ is nearly vertical. These diagrams were obtained when the core had been well demagnetized. Figure 54 shows similar diagrams for direct curves (dotted) and for reverse curves (full).

THE GROWTH OF THE INDUCTION FLUX IN THE CORE OF AN ELEC-TROMAGNET WHILE THE EXCITING CURRENT IS TEMPORARILY CONSTANT.

It sometimes happens that if a number of secondary coils of low resistance, wound upon the core of an electromagnet, are closed on themselves, the building-up curve of a current in the exciting coil is for a comparatively long time almost exactly parallel to the time axis. During this time it is difficult to detect any change in the intensity of the current, and yet the flux of magnetic induction through the core is increasing at a very nearly constant rate. This fact, which has a certain pedagogic interest, is easily illustrated. The curve



Direct and reverse current curves for a transformer with a laminated core. The existence of eddy currents is clearly shown.

OPQU (Figure 55) shows a nearly typical case, and the line OKLG represents on a different scale the induced current in one of the secondary circuits. To a person watching an amperemeter in the primary circuit, the current seems to have attained its final value in less than a second, and if he leaves the instrument at the end of, say, five seconds, he feels sure that the current has become steady. Meanwhile the induction flux, as measured on the scale of the diagram by the area between the curve and the line YU (or, on a different scale, by the area under the curve OKLG), is constantly growing. Of course if the core is very large, the whole building-up time may be a minute or more, and the phenomenon may then become very striking.

The magnet T has three coils. The first (A) has 750 turns, the

second (B) 250 turns, and the third (C), which is made of wire of very large cross-section, has a small unknown number. Figure 56 reproduces accurately the records of two oscillographs, one in the coil A, the other in B, when C was closed. OMQL is a part of the building-up curve for the main circuit (A), and Ocbk is a corresponding portion of the record of the induced current in B. In the case represented by the full line OMQTVW, the coil C was suddenly opened at about 1.05 seconds after the start: Ocbznda shows the record of the induced current in B under these circumstances. The scales of the two oscillographs were, of course, not the same. The sudden jumps in the oscillograms might have been predicted, in amount as well as in direction, by the principle of the "Conservation of Electromagnetic Mo-

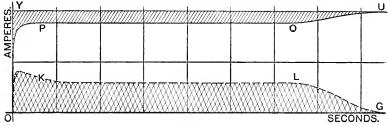


FIGURE 55.

menta." We shall return to the subject of the sudden changes brought about in the currents in inductively connected circuits when the inductances of the system are impulsively changed.

THE EFFECTIVENESS OF FINE SUBDIVISION IN THE CORE OF AN ELECTRO-MAGNET FOR THE PREVENTION OF ELECTROMAGNETIC DISTURBANCES DUE TO EDDY CURRENTS, WHEN A STEADY ELECTROMOTIVE FORCE IS APPLIED TO THE CIRCUIT OF THE EXCITING COLL.

In order to determine approximately the magnitude of the effect of eddy currents upon the growth of a current <sup>13</sup> in the coil of an electromagnet the core of which is made of fine iron wire, we may consider the case of a very long solenoid consisting of N turns of wire per centimeter of its length, wound closely about a long prism of square cross-

<sup>13</sup> The influence of eddy currents in the formation of a regularly fluctuating current in the exciting coil of a transformer under a given, alternating electromotive force has been studied by J. J. Thomson for cores of square cross-suction built up of iron sheets, and by Heaviside for round cylindrical cores cut radially. See the Electrician for April, 1892, and Heaviside's Electrical Papers, 1. xxviii.

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section  $(2 \ a \times 2 \ a)$  built up uniformly (Figures 59 and 60) of a large number of varnished filaments of square cross-section  $(c \times c)$ , or else consisting of a bundle of infinitely long straight wires. The axis of the prism shall be the z axis, and the x and y axes shall be parallel to faces of the prism. The electric resistance of the solenoid per centimeter of its length shall be w, the constant applied electromotive force per centimeter of the length of the prism shall be E, and the intensity of the current in the coil shall be C. Within the core, the magnetic field (H) will have the direction of the z axis, and if q is the current flux at any place

 $4\pi q = \text{Curl } H,\tag{27}$ 

or

$$4\pi q_x = \frac{\partial H}{\partial y}, \quad 4\pi q_y = -\frac{\partial H}{\partial x}, \quad 4\pi q_z = 0.$$

Within any filament of iron in the core, H satisfies the equation

$$\frac{\hat{\epsilon}H}{\hat{\epsilon}t} = \frac{\rho}{4\pi\mu} \left( \frac{\hat{\epsilon}^2 H}{\hat{\epsilon}x^2} + \frac{\hat{\epsilon}^2 H}{\hat{\epsilon}y^2} \right),\tag{28}$$

where  $\rho$  is the specific resistance of the iron and  $\mu$  is its permeability, which for the present purpose shall be regarded as having a fixed value.

When there are no Foucault currents in the core, the intensity (H) of the magnetic field within has at every point the boundary value  $H_S$  or  $4\pi NC$ , but if positively directed eddy currents exist, H may be greater at inside points than at the surface. We need not distinguish between the flux p through the turns of the coil per centimeter of its length, and N times the induction flux  $\mu \int \int H dx \, dy$  through the core, so that we may write

$$E - \frac{dp}{dt} = E - \mu N \int \int \frac{\partial H}{\partial t} \cdot dx \, dy = w \cdot C = \frac{w \cdot H_s}{4 \pi N}, \tag{29}$$

or by virtue of (28),

$$E = \frac{w \cdot H_s}{4 \pi N} + \frac{\mu \rho N}{4 \pi \mu} \int \int \left( \frac{\hat{\sigma}^2 H}{\hat{c}_{\ell} r^2} + \frac{\hat{c}^2 H}{\hat{c}_{\ell} g^2} \right) dx \, dy, \tag{30}$$

where the integration extends over a cross-section of the core.

The vector H is always perpendicular to its curl, and the intensity of the component of the current at any point in the iron, in any direc-

tion, s, parallel to the xy plane at any instant, is equal to  $1/4 \pi$  times the value at that point, at that instant, of the derivative of H in a direction parallel to the xy plane, and 90° in counter clockwise rotation ahead of s.

Along any curve in the iron parallel to the xy plane, H must be constant if there is no flow of electricity across the curve. At every instant, therefore, the value of H at the boundary common to any two filaments must be everywhere equal to  $H_s$ . If the coil circuit is broken, H must be constantly zero at the surface of every filament.

Two or three general theorems concerning solutions of differential equations of the form

$$y\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2}\right) = \frac{\partial w}{\partial z},$$

will be helpful to us.

If v and w represent any analytic functions of x, y, z, and if L(w), M(v) represent the adjoint differential expressions

$$g \cdot \frac{\partial^2 w}{\partial x^2} + g \cdot \frac{\partial^2 w}{\partial y^2} - \frac{\partial w}{\partial z}, \tag{31}$$

$$g \cdot \frac{\hat{c}^2 r}{\hat{c} x^2} + g \cdot \frac{\hat{c}^2 v}{\hat{c} y^2} + \frac{\hat{c} v}{\hat{c} z}, \tag{32}$$

the corresponding form of the generalized Green's Theorem may be expressed by the equation,

$$\iiint \left[ v \cdot L(w) - w \cdot M(v) \right] \cdot dx \, dy \, dz = 
g \iint \left( v \cdot \frac{\partial w}{\partial x} - w \cdot \frac{\partial v}{\partial x} \right) \cdot \cos(x, n) \cdot dS + 
g \iint \left( v \cdot \frac{\partial w}{\partial y} - w \cdot \frac{\partial v}{\partial y} \right) \cdot \cos(y, n) \cdot dS - \iint w \cdot \cos(z, n) \cdot dS; \quad (33)$$

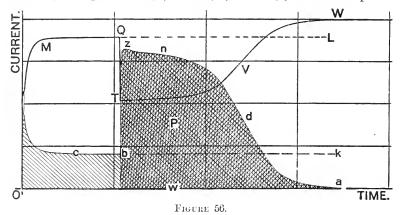
and it is easy to prove that

$$\iiint r \cdot L(w) \, dx \, dy \, dz = g \iint r \left( \frac{\partial w}{\partial x} \cdot \cos(x, u) + \frac{\partial w}{\partial y} \cdot \cos(y, u) \right) dS$$
$$- y \iiint \left( \frac{\partial w}{\partial x} \cdot \frac{\partial v}{\partial x} + \frac{\partial w}{\partial y} \cdot \frac{\partial r}{\partial y} \right) dx \, dy \, dz - \iiint \cdot \frac{\partial w}{\partial z} \cdot dx \, dy \, dz. \quad (34)$$

If w and v are identically equal, the last equation becomes

$$\iiint w \cdot L(w) \cdot dx dy dz = g \iint w \left( \frac{\partial w}{\partial x} \cdot \cos(x, n) + \frac{\partial w}{\partial y} \cdot \cos(y, n) \right) dS$$
$$- : \iiint \left[ \left( \frac{\partial w}{\partial x} \right)^2 + \left( \frac{\partial w}{\partial y} \right)^2 \right] dx dy dz - \frac{1}{2} \iint w^2 \cdot \cos(z, n) dS. \tag{35}$$

(I) If  $S_0$  is a closed cylindrical surface the generating lines of which are parallel to the z axis, and if  $\Omega$ ,  $\Omega'$  — two functions which within  $S_0$  satisfy the equations  $L(\Omega) = 0$ ,  $L(\Omega') = 0$  — (1) vanish at all points



of  $S_0$  and at all points within  $S_0$  for which z is positively infinite, and (2) have the given constant value  $\Omega_0$  at all points in the xy plane within  $S_0$ ; then if we apply (35) to the difference between  $\Omega$  and  $\Omega'$ , using as a field of volume integration the space inside  $S_0$  on the positive side of the xy plane (Figure 57), we shall learn that in this space  $\Omega$  and  $\Omega'$  must be identically equal. The value of  $\Omega$  within  $S_0$  is in no way affected by conditions which a physical extension of the function might be required to satisfy outside  $S_0$ .

- (II) If  $S_0$  is a closed cylindrical surface, the generating lines of which are parallel to the z axis, if W is a function which within  $S_0$  satisfies the equation L(W) = 0, and if
- (1) W and  $\partial W/\partial z$  vanish at all points within and on  $S_0$  for which z is positively infinite,
- (2) W has a given constant value ( $W_0$ ) at all points on the xy plane within  $S_0$ .

(3) W on  $S_0$  is a function  $(W_s)$  of z only, such that if n indicates the direction of the external normal to  $S_0$ 

$$W_s + k \int \left(\frac{\partial W}{\partial u}\right) ds = 0, \tag{36}$$

where k is a given positive constant, and the line integral is to be taken around the perimeter of a right section of  $S_0$  made by the plane z=z; and, hence, if

(4)  $\iiint \left(\frac{\partial W}{\partial z}\right) dS$ , taken over so much of the xy plane as lies within  $S_0$ , is given, then W is uniquely determined.

If we assume that two different functions (W, W') may satisfy all these conditions, and denote their difference by u,

$$L(u) = 0$$
, within  $S_0$ ,

u and  $\partial u/\partial z$  vanish at all points within  $S_0$ , for which z is positively infinite,

u vanishes at all points on the xy plane within  $S_0$ 

u on  $S_0$  satisfies the equation

$$u_s + k \int \left(\frac{\partial u}{\partial u}\right) ds = 0.$$
 (37)

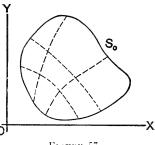


Figure 57.

If we use the space bounded by  $S_0$ , the xy plane, and the plane  $z = \infty$ , as a field of volume integration, and denote the whole boundary by  $S_i$ ; then, since  $\cos(z, n)$  vanishes on  $S_0$ , and u,  $\cos(x, n)$ ,  $\cos(y, n)$ , vanish on the portions of the planes z = 0,  $z = \infty$  used as boundaries, (35) yields the equation

$$\iiint \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 \right] dx \, dy \, dz = \iint u_S \cdot \frac{\partial u}{\partial n} \cdot dS_0. \tag{38}$$

Now u has the same value at all points on the perimeter (s) of any right section of  $S_{ij}$  so that

$$\iint u_s \cdot \frac{\partial u}{\partial n} \cdot dS_0 = \int_0^\infty u_s \cdot dz \int \frac{\partial u}{\partial n} \cdot ds = -\frac{1}{k} \int_0^\infty u_s^2 \cdot dz, \qquad (39)$$

and (38) becomes

$$\iiint \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 \right] dx dy dz + \frac{1}{k} \int_0^\infty u_s^2 \cdot dz = 0, \quad (40)$$

where k is intrinsically positive; but each of these last integrals has an integrand that must be either zero or positive at every point in its domain, so that u must be independent of x and y, and must vanish on  $S_0$  at every point. It follows that u is everywhere zero and that W = W'.

It is evident that the condition (3) might have been stated in the form of the equation

$$W_s + k \int \int \left( \frac{\hat{c}^2 W}{\hat{c}_{x'}^2} + \frac{\hat{c}^2 W}{\hat{c}_{y'}^2} \right) dA = 0, \tag{41}$$

where the integration is to be extended over so much of the plane z = z as lies within  $S_0$ .

If the space within  $S_0$  were cut up into portions (filaments) by the cylindrical surfaces  $S_1, S_2, S_3, \cdots$ , the generating lines of which were



FIGURE 58.

parallel to the z axis, and if within each filament L(W) vanished, while, in addition to the other requirements enumerated above, W were constrained to have at every point of the surface of every filament the value  $(W_s)$ , which points with the same z coordinate on the surface  $\aleph_0$  had, — though the normal derivative of W at the common surface of two filaments were not expected to be continuous, — we might assume as before that two different functions

could satisfy all these conditions and denote their difference by u. We could then apply (35) to every filament separately (Figures 57 and 58) and obtain from each an equation of the form

$$\int u_{S} \cdot dz \int \int \left( \frac{\partial^{2} u}{\partial x^{2}} + \frac{\partial^{2} u}{\partial y^{2}} \right) dB - \int \int \int \left[ \left( \frac{\partial u}{\partial x} \right)^{2} + \left( \frac{\partial u}{\partial y} \right)^{2} \right] dz dB = 0$$
(42)

where B denotes a cross-section of the filament. If, then, all these equations were added together, the resulting equation would be

$$\int u_{s} \cdot dz \int \int \left( \frac{\hat{c}^{2} u}{\hat{c} x^{2}} + \frac{\hat{c}^{2} u}{\hat{c} y^{2}} \right) dA - \int \int \int \left[ \left( \frac{\hat{c} u}{\hat{c} x} \right)^{2} + \left( \frac{\hat{c} u}{\hat{c} y} \right)^{2} \right] dz dA = 0,$$
(43)

which is (35). In this case also, therefore, W is determined.

- (III) If  $S_0$  is a closed cylindrical surface the generating lines of which are parallel to the z axis, if V is a function which within  $S_0$  satisfies the equation L(V) = 0, and if
- (1)  $\Gamma$  and  $\partial V/\partial z$  vanish at all points within and on  $S_0$  for which z is positively infinite,
- (2) V has a given constant value ( $V_0$ ) at all points on the xy plane within  $S_0$ ,
- (3) V on  $S_0$  is a function  $(V_S)$  of z only, such that, if n indicates the direction of the external normal to  $S_0$

$$V_{s} + l \cdot \frac{dV_{s}}{dz} + k \int \left(\frac{\partial V}{\partial n}\right) ds = 0,$$

$$V_{s} + l \cdot \frac{dV_{s}}{dz} + k \int \int \left(\frac{\partial^{2} V}{\partial x^{2}} + \frac{\partial^{2} V}{\partial y^{2}}\right) dx \, dy = 0,$$
(44)

or

where l and k are given positive constants, the line integral is to be taken around the perimeter (s) of a right section of  $S_0$  made by the plane z = z, and the double integral over the section; then V is uniquely determined.

(IV) Let  $S_0$  be a closed cylindrical surface which completely surrounds (Figure 58) several other mutually exclusive, closed cylindrical surfaces  $(S_1, S_2, S_3, \cdots)$  the generating lines of which are parallel to those of  $S_0$  and to the z axis; and let the intersections of these surfaces with the plane z = z be denoted by  $S_0, S_1, S_2, S_3, \cdots$ . Let the portions of the plane z = z within  $S_1, S_2, S_3, \cdots$ , be denoted by  $A_1, A_2, A_3, \cdots$ , and the portion within  $S_0$  but outside  $S_1, S_2, S_3, \cdots$ , be denoted by  $A_n$ . Let  $\tau_0, \tau_1, \tau_2, \tau_3, \cdots$ , represent the volumes of the prisms (bounded by the planes  $z = 0, z = \infty$ ) of which the cross-sections made by the planes z = z are  $A_0, A_1, A_2, A_3, \cdots$ .

In the regions  $\tau_0$ ,  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$ ,  $\cdots$ , let the scalar function U satisfy the equations

$$\frac{\partial U}{\partial z} = g_0 \left( \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} \right),$$

$$\frac{\partial U}{\partial z} = g_1 \left( \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} \right),$$

$$\frac{\partial U}{\partial z} = g_2 \left( \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} \right).$$
(45)

where  $g_0$ ,  $g_1$ ,  $g_2$ ,  $g_3$  are given positive constants, and let the value ( $U_3$ ) of U on the cylindrical surfaces be a function of z only (the same for all the surfaces), such that

$$U_{S} + k_{0} \int \int \left( \frac{\partial^{2} I'}{\partial x^{2}} + \frac{\partial^{2} I'}{\partial y^{2}} \right) dA_{0} + k_{1} \int \int \left( \frac{\partial^{2} I'}{\partial x^{2}} + \frac{\partial^{2} U}{\partial y^{2}} \right) dA_{1}$$

$$+ k_{2} \int \int \left( \frac{\partial^{2} I'}{\partial x^{2}} + \frac{\partial^{2} I'}{\partial y^{2}} \right) dA_{2} + \dots = 0,$$

$$(46)$$

where  $k_0$ ,  $k_1$ ,  $k_2$ ,  $k_3$  are given positive constants. Then if U has the constant value  $U_0$  at all points in so much of the xy plane as lies within  $S_0$  and the value zero at all points on and within  $S_0$  for which z is positively infinite, U is determined in the positive space within  $S_0$ . For if we assume that there could be two such functions and apply (35) to their difference (u) in each of the regions  $\tau_0$ ,  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$ ,  $\cdots$ , multiply the resultant equations by  $k_0$ ,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $\cdots$ , and add them together, it will be easy — to show in the way indicated under (II) — that u is zero everywhere inside  $S_0$  on the positive side of the xy plane.

It is to be remembered that

$$\frac{\partial^2 I'}{\partial x^2} + \frac{\partial^2 I'}{\partial y^2} \tag{47}$$

is an invariant of a transformation of orthogonal Cartesian co-ordinates in the xy plane.

(V) In an important special case similar to that stated in (IV),  $k_1, k_2, k_3, \dots$ , are all equal,  $g_1, g_2, g_3, \dots$ , are all equal, and all the  $n^2$  areas  $A_1, A_2, A_3, \dots$ , are alike in form, however they may be oriented. In the region  $\tau_0$ , U is everywhere equal to  $U_s$ , which is, as before, a function of z only, and the surface condition becomes

$$U_{s} + l \cdot \frac{dU_{s}}{dz} + k \sum_{m} \int \int \left( \frac{\partial^{2} U}{\partial x^{2}} + \frac{\partial^{2} U}{\partial y^{2}} \right) lA_{m}, \tag{48}$$

where l and k are given positive constants.

If in this case we find for every one  $(\tau_m)$  of the regions  $\tau_1, \tau_2, \tau_3, \cdots$ , the function  $(ic_m)$ , which within  $(\tau_m)$  satisfies the equation

$$\frac{\partial w_m}{\partial z} = q \left( \frac{\partial^2 w_m}{\partial x^2} + \frac{\partial^2 w_m}{\partial y^2} \right), \tag{49}$$

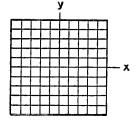
and at the boundary the surface condition

$$w_S + l \cdot \frac{dw_S}{dt} + n^2 k \int \int \left( \frac{\partial^2 w_m}{\partial x^2} + \frac{\partial^2 w_m}{\partial y^2} \right) L \mathbf{f}_m = 0, \tag{50}$$

and which has the given constant value  $U_0$  on so much of the xy plane as lies within  $S_0$  and the value zero when z is infinite, and if we assign to the function without  $S_m$  where it is not defined, the value zero, then, apart from differences of orientation, all these functions will be alike. If after this we define a function within  $S_0$  by assigning to it within every one of the regions  $\tau_1, \tau_2, \tau_3, \cdots$ , the same value as the w function belonging to this region, and give to it in  $\tau_0$  the common value  $w_s$ , the function thus determined will be the unique function U described above.

If after a steady current of intensity E/w has been running for some time in the coil of the solenoid under consideration, so that the mag-

netic field within the core (which in this case shall be built up, in the manner shown in Figure 59, of filaments of square cross-sections) has everywhere the given constant value  $H_0$ , the coil circuit be very suddenly broken, the value of H falls instantly, not only at the outer surface of the prism, but also at the surface of every filament, to zero. Inside every filament



$$\frac{\partial H}{\partial t} = \frac{\rho}{4\pi u} \left( \frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} \right). \tag{51}$$

When t = 0,  $H = H_0$  everywhere within the iron, and when t is infinite, the field intensity is everywhere zero. According to (I), therefore, we may consider every filament by itself.

If we seek a solution of the equation (51) which shall be of the form  $X \cdot Y \cdot T$ , where X involves x alone, Y involves y alone, and T is a function of t alone, we shall obtain the expressions

$$X = A_1 \cdot \cos \alpha x + A_2 \cdot \sin \alpha x, \quad Y = B_1 \cdot \cos \beta y + B_2 \cdot \sin \beta y, \quad T = e^{-\lambda^2 t},$$
(52)

where

$$\lambda^2 = \frac{\rho\left(\alpha^2 + \beta^2\right)}{4\pi\mu} \,. \tag{53}$$

If we use as normal function the product

$$A_{mn} \cdot e^{-\lambda^2 t} \cdot \sin \frac{m\pi x}{c} \cdot \sin \frac{n\pi y}{c},\tag{54}$$

where  $\lambda^2 = \pi \rho (m^2 + n^2)$  (4  $\mu c^2$ ) and m and n are positive integers, and write

$$H = \sum_{m=1}^{m=\infty} \sum_{n=1}^{n=\infty} A_{mn} \cdot e^{-\lambda^2 t} \cdot \sin \frac{m\pi x}{c} \cdot \sin \frac{n\pi y}{c}, \tag{55}$$

this expression will satisfy all conditions if  $A_{mn}$  be so taken that when t=0, the second number of the equation shall be equal to  $H_0$  for all values of x and y within the filament. We have, therefore, the equation  $^{14}$ 

$$A_{mn} = \frac{4H_0}{c^2} \int_0^c d\chi \int_0^c \sin\frac{m\pi\chi}{c} \cdot \sin\frac{n\pi\psi}{c} d\psi \tag{56}$$

and

$$A_{mn} = \frac{16}{\pi^2} \frac{H_0}{mn}$$

when m and n are both odd;

$$A_{mn} = 0$$
,

when either m or n is even, so that

$$H = \frac{16 H_0}{\pi^2} \sum_{j=0}^{j=\infty} \sum_{k=0}^{k=\infty} \frac{e^{-\lambda^2 t}}{(2j+1)(2k+1)} \cdot \sin \frac{(2k+1)\pi x}{c} \cdot \sin \frac{(2j+1)\pi y}{c}$$
(57)

$$\lambda^2 = \frac{\pi \rho}{4 \,\mu c^2} [(2 \,k + 1)^2 + (2 \,j + 1)^2]. \tag{58}$$

From (58) it appears that the whole flux of magnetic induction through the core at the time t is

$$\phi = \frac{64 \cdot \mu \cdot H_0 \cdot c^2}{\pi^4} \sum_{j=1}^{j=\infty} \sum_{k=1}^{k=\infty} \frac{e^{-\lambda^2 t}}{(2j+1)^2 (2k+1)^2},$$
 (59)

or, if 
$$g = \pi \rho/4 \,\mu c^2,$$

<sup>&</sup>lt;sup>14</sup> Byerly, Treatise on Fourier's Series, etc., § 71. Riemann-Weber, Die partiellen Differential-gleichungen der mathematischen Physik, Bd. II, § 99.

$$\phi = \frac{64 \cdot \mu \cdot H_0 \cdot c^2}{\pi^4} \sum_{j=1}^{j=\infty} \frac{e^{-g(2j+1)^2 l}}{(2j+1)^2} \sum_{k=1}^{k=\infty} \frac{e^{-g(2k+1)^2 l}}{(2k+1)^2}$$
(60)

In these equations absolute electromagnetic units are to be used, and for good soft iron we may assume that  $\pi\rho/4$  is very approximately equal to 8000. It is evident that for different values of c when  $\mu$  is given,  $e^{-\lambda^2 t}$  will have the same numerical value for values of t proportional to  $c^2$ ; for instance, if c = 20, t = 10,  $e^{-\lambda^2 t}$  will have the same value as it would if c were 1 and t, 1/40. If c is fixed,  $e^{-\lambda^2 t}$  will have the same value for values of t proportional to  $\mu$ .

It is possible to show that if c=1 and  $\mu=200$ , — to take a special case, — the series

$$S \equiv \sum_{k=0}^{k=\infty} \frac{e^{-g(2k+1)^2 t}}{(2k+1)^2} \tag{61}$$

has at different times the approximate values given in the following table:

|        | t.                                             | S.                                                                                                                     |
|--------|------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|
| 1.2337 | 0.01000                                        | 0.6734                                                                                                                 |
| 1.1450 | 0.02000                                        | 0.4494                                                                                                                 |
| 1.1084 | 0.02500                                        | 0.3679                                                                                                                 |
| 1.0565 | 0.05000                                        | 0.1353                                                                                                                 |
| 0.9830 | 0.07500                                        | 0.04979                                                                                                                |
| 0.9534 | 0.10000                                        | 0.01832                                                                                                                |
| 0.8374 | 0.20000                                        | 0.00034                                                                                                                |
|        | 1.1450<br>1.1084<br>1.0565<br>0.9830<br>0.9534 | 1.1450     0.02000       1.1084     0.02500       1.0565     0.05000       0.9830     0.07500       0.9534     0.10000 |

TABLE V.

From the numbers in this table it is easy to compute, for cores of square cross-section, the fractional part of the original induction flux through the core which remains after the circuit of the exciting coil has been broken for a given time. For a solid core, the area of the square section of which is 100 square centimeters, the results are given in the next table, when  $\mu$  is 200.

If the core were built up compactly of varnished square rods of one square centimeter in cross-section, the times in the table should be

divided by 100, and if the core were made up of 10,000 slender filaments, the flux would sensibly disappear during the first thousandth of a second. It is easy to get similar results for any other value of  $\mu$ .

| Time in Seconds<br>after the Breaking<br>of the Circuit. | Fractional Part<br>of Original Flux<br>still remaining. | Time in Seconds<br>after the Breaking<br>of the Circuit. | Fractional Part<br>of Original Flux<br>still remaining. |
|----------------------------------------------------------|---------------------------------------------------------|----------------------------------------------------------|---------------------------------------------------------|
| 0.000                                                    | 1.000                                                   | 1.000                                                    | 0.298                                                   |
| 0.025                                                    | 0.861                                                   | 2.000                                                    | 0.133                                                   |
| 0.050                                                    | 0.807                                                   | 2.500                                                    | 0.089                                                   |
| 0.100                                                    | 0.733                                                   | 5.000                                                    | 0.012                                                   |
| 0.200                                                    | 0.635                                                   | 7.500                                                    | 0.0016                                                  |
| 0.250                                                    | 0.597                                                   | 10.000                                                   | 0.0002                                                  |
| 0.500                                                    | 0.461                                                   |                                                          |                                                         |

TABLE VI.

If the cross-section of the core were a circle of radius a, and if, after a uniform magnetic field of strength  $H_0$  had been established in the core the exciting circuit were suddenly broken, the intensity of the field at any time, at any point distant r centimeters from the axis would be given by the expression  $^{15}$ 

$$H = \frac{2H_0}{\alpha} \cdot \sum_{k} \frac{J_0(n_k \cdot r)}{n_k \cdot J_1(n_k \cdot \alpha)} e^{-\beta_k^2 t}$$
 (62)

where  $\beta^2 = \rho n^2/4 \pi \mu$  and the whole flux through the core would be

$$2\pi\mu \int_{0}^{a} Hr dr \text{ or } 4\pi\mu H_{0} \sum_{k=1}^{\infty} \frac{e^{-\beta_{k}^{3}l}}{n_{k}^{2}}$$
 (63)

In these equations  $n_k a$  is the kth root in order of magnitude of the Bessel's Equation

$$J_{\theta}(na) = 0. ag{64}$$

<sup>&</sup>lt;sup>15</sup> Heaviside, Electrical Papers, 1, xxviii. Peirce, These Proceedings, 41, 1906. Byerly, Treatise on Fourier's Series, etc., p. 229.

The first ten roots are as follows:

TABLE VII.

| na.       | k.                                            | na.                                                                                          |
|-----------|-----------------------------------------------|----------------------------------------------------------------------------------------------|
| 2.404826  | 6                                             | 18.071064                                                                                    |
| 5.520078  | 7                                             | 21.211637                                                                                    |
| 8.653728  | 8                                             | 24.352472                                                                                    |
| 11.791534 | 9                                             | 27.493479                                                                                    |
| 14.930918 | 10                                            | 30.634606                                                                                    |
|           | 2.404826<br>5.520078<br>8.653728<br>11.791534 | 2.404826       6         5.520078       7         8.653728       8         11.791534       9 |

From these numbers the  $\beta$ 's can be found, and then from (63) the flux in the core after any interval. When the time is short, the series converges very slowly, and the computation is long and troublesome, but for relatively large values of t the work is not difficult.

The next table shows the fractional part  $(\Omega)$  of the original flux remaining in a core, the cross-section of which is a circle of 20 centimeters diameter, and in which  $\mu$  is 200; 1 second, 4 seconds, and 8 seconds after the breaking of the exciting circuit: the corresponding fraction for a core of square cross-section (20 cms.  $\times$  20 cms.) is given for comparison. The actual value of the original flux is of course a little larger in the second case because the area of the cross-section is greater.

TABLE VIII.

| t. | $\Omega$ for the Round Core. | Ω for the<br>Square Core. |
|----|------------------------------|---------------------------|
| 1  | 0 588                        | 0.597                     |
| 4  | 0.270                        | 0.298                     |
| 8  | 0.106                        | 0.133                     |

After 16 seconds  $\Omega$  for the round core would be 0.016. In the case of a round core of exactly the same cross-section area as the square solid core, and the same original flux, the fractional part remaining after one second would be 0.630.

If the square core of the solenoid — the area of the cross-section of which is A square centimeters — be made of a bundle of infinitely long,

straight iron wires, placed close together (Figure 60), and if, after a steady current of intensity E/w has been running for some time through



FIGURE 60.

the solenoid, so that there is a magnetic field of uniform intensity  $H_0=4\,\pi NE/w$  in the core, the applied electromotive force be suddenly shunted out of the solenoid circuit, the current (C) in the coil will gradually die out. At any instant the field, in so much of the space A as is occupied by air, is  $4\,\pi NC$ , for eddy currents in the wires act like solenoid sheets and do not affect the field without the wires. Within each wire there are

eddy currents, of course, and at every point in the wire, at every instant, the field intensity, H, must satisfy the equation

$$\frac{\partial H}{\partial t} = \frac{\rho}{4\pi\mu} \left[ \frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} \right]$$
 (65)

The induction flux through the turns of the solenoid per centimeter of its length shall be p, so that

$$E - \frac{dp}{dt} = wC$$
, or, in this case,  $\frac{dp}{dt} = -wC$ .

If there are  $n^2$  wires in the core and the area of the cross-section of each of them is B,

$$p = 4\pi N^2 C(A - n^2 B) + \mu N \iint H \cdot dx \, dy \tag{66}$$

where the double integral is to be extended over the cross-sections of all the wires; hence

$$wC + (A - n^2B) 4\pi N^2 \cdot \frac{dC}{dt} + \mu N \int \int \frac{\partial H}{\partial t} \cdot dx \, dy = 0; \quad (67)$$

and if the wires fill the square space as full as possible,

$$A - n^2 B = 0.2146 A$$
, nearly.

If  $H_s$  represents the strength of the magnetic field in the air space within the solenoid,

$$H_S + \frac{4\pi N^2}{w} (A - n^2 B) \frac{dH_S}{dt} + \frac{4\pi\mu N^2}{w} \iint \frac{\partial H}{\partial t} \cdot dx \, dy = 0.$$
 (68)

The function H thus defined falls under theorem (V) above, and it is evident that we ought to seek, for a single wire, a function  $\varpi$  which within the wire shall satisfy (65), at the surface shall fulfil the condition

$$\boldsymbol{\omega}_{S} + \frac{4\pi N^{2}}{w} (A - n^{2}B) \frac{d\boldsymbol{\omega}_{S}}{dt} + \frac{4\pi\mu n^{2}N^{2}}{w} \int \int \frac{\partial \boldsymbol{\omega}}{dt} \cdot dx \, dy = 0, \quad (69)$$

and which when t = 0 shall have the value  $H_0$  and when t is infinite, the value zero. When we have to deal with a single wire of radius b (= a/n) alone, it is obviously convenient to use polar co-ordinates with origin at the point where the axis of the wire cuts the xy plane, and if we do this (65) and (67) take the forms

$$\frac{\hat{c}\varpi}{\partial t} = \frac{\rho}{4\pi\mu r} \cdot \frac{\hat{c}}{\hat{c}r} \left[ r \cdot \frac{\hat{c}\varpi}{\hat{c}r} \right],\tag{70}$$

$$\boldsymbol{\omega}_{s} + \frac{4\pi N^{2}}{w} (A - n^{2}B) \frac{d\boldsymbol{\omega}_{s}}{dt} + \frac{2\pi n^{2}N^{2}\rho b}{w} \left(\frac{\hat{c}\boldsymbol{\omega}}{\hat{c}r}\right)_{r=b} = 0, \quad (71)$$

or

$$\varpi_S + l \cdot \frac{d\varpi_S}{dt} + kn^2 b \left(\frac{\hat{c}\varpi}{\hat{c}r}\right)_{r=b} = 0,$$
(72)

where l, k, n, and b are given, positive constants.

If we attempt to find a solution of (70) in the form of the product of a function of t, and a function of r, we arrive, of course, at the normal form

$$e^{-\beta^2 t} \left[ L \cdot J_0(mr) + M \cdot K_0(mr) \right], \tag{73}$$

but Bessel's Functions of the second kind will not be needed here, and we may write, M = 0,

$$\boldsymbol{\varpi} = \sum_{m} L_m \cdot e^{-\beta^2 t} \cdot J_0(mr), \tag{74}$$

where either m or  $\beta$  may be assumed at pleasure and the other computed from the equation

$$m^2 \rho = 4 \,\pi \mu \beta^2. \tag{75}$$

If for m in the equation (74) we use the successive roots of the transcendental equation

$$J_0(mb) = \frac{kn^2 \cdot mb}{1 - l\beta^2} \cdot J_1(mb) \tag{76}$$

the series will satisfy (70) and (72), and if the coefficients can be so chosen as to make

$$\sum_{0}^{\infty} L_m \cdot J_0(mr) = H_0 \tag{77}$$

equation (74) will give the function sought.

Although the development (77) is not one of those for which the coefficients can be found by the usual devices, it is easy to solve the problem, for such cases as are of practical interest, to any desirable approximation.

We shall find it instructive, however, to inquire first what the solution would be if the second term of (72) were lacking, for, in view of the fact that the permeability of the iron is relatively large compared with that of the air, it seems likely that in some instances, where the series is very convergent, this modified problem and the real one will have nearly equal numerical answers.

We have, then, so to choose  $L_m$ ,  $\beta$ , and m, subject to (75) that the value of the series (77) shall be  $H_0$  when t=0, for all values of r up to b; and that at every instant

$$\sigma_s + \frac{2\pi n^2 N^2 \rho}{w} \left(\frac{\partial \sigma}{\partial r}\right)_{r=b} = 0.$$
 (78)

It is necessary, therefore, that m shall be a root of the transcendental equation

$$J_0(mb) = \frac{2\pi N^2 n^2 \rho}{w} \cdot mb \cdot J_1(mb), \tag{79}$$

which may be written in other forms by virtue of the relations

$$\frac{dJ_0(x)}{dx} = -J_1(x), \qquad \int_0^x x \cdot J_0(x) \, dx = x \cdot J_1(x). \tag{80}$$

It will be convenient to illustrate the effect of making b small (and therefore n large) while a is kept constant, by a numerical example. Let us assume that the cross-section of the solenoid is a square of 10 centimeters side-length, so that a=5; let the solenoid have 10 turns of insulated wire per centimeter of its length, and let the resistance of these 10 turns be  $\frac{1}{16}$ th of an ohm, so that in absolute units  $w=10^9/16$ . If, then, we take the specific resistance of the core to be  $(10^6/32\pi)$ 

absohms at the room temperature (Fleming and Dewar),  $2\pi N^2 \rho/w$  will be equal to  $\frac{1}{10}$ , and the equation for m takes the form

$$J_{0}(mb) = \frac{n^{2}}{10}(mb) \cdot J_{1}(mb) = \frac{mb}{\lambda} \cdot J_{1}(mb). \tag{81}$$

But 16

$$1 = \sum_{k=0}^{\infty} \frac{2\lambda \cdot J_0(mr)}{(\lambda^2 + m^2b^2)J_0(mb)},$$
 (82)

and hence

$$\boldsymbol{\varpi} = 2 \, \lambda H_0 \sum_{m} \frac{e^{-\beta^2 t} \cdot J_0(mr)}{(\lambda^2 + m^2 b^2) J_0(mb)}. \tag{83}$$

The whole flux of magnetic induction through the iron of the core is then  $\mu n^2$  times the integral of  $\varpi$  taken over the circle of radius b in which  $\varpi$  is defined; that is

$$\phi = 4 \pi \mu \lambda H_0 n^2 b \sum_{m(\lambda^2 + m^2 b^2)} \frac{e^{-\beta^2 t} \cdot J_1(mb)}{m(\lambda^2 + m^2 b^2) J_0(mb)},$$
 (84)

or

$$\phi = 4 \pi \mu \lambda^2 H_0 n^2 \sum_{n=0}^{\infty} \frac{e^{-\beta^2 t}}{m^2 (\lambda^2 + m^2 b^2)}.$$
 (85)

Since  $\lambda = 10/n^2$ , the coefficient of the series may be written 400  $\pi \mu H_0/n^2$ , and we may assume that  $\mu = 100$ .

The time rate of change of the total induction flux through the turns of the solenoid, per centimeter of its length, is

$$\frac{9950 \cdot 10^4 \cdot H_0}{n^2} \sum_{k=0}^{\infty} \frac{e^{-\beta^2 t}}{\lambda^2 + m^2 b^2}$$
 (86)

If the square core is built up of 100 circular rods, each 1 centimeter in diameter,  $n^2 = 100$ ,  $\lambda = 1/10$ , and the m's are defined by the equation

$$J_0(mb) = 10 \, mb \cdot J_1(mb) \tag{87}$$

in which b = 1/2.

It is not difficult to show by trial and error from Meissel's tables <sup>17</sup> that the first five roots of this equation have values approximately equal to those given in the following table:

Byerly, Treatise on Fourier's Series, etc., p. 229.

<sup>&</sup>lt;sup>17</sup> Meissel, Tafel der Bessels'schen Functionen, Berliner Abhandlungen, 1888; Gray and Mathews, Treatise on Bessel's Functions, pp. 247-266; Peirce and Willson, Bulletin of the American Mathematical Society, 1897.

| TABLE    | IX    |
|----------|-------|
| 11111111 | * * * |

| $m_1b = 0.44168$ | $\log \beta_1{}^2 = 0.79077$ | $m_1^2 = 0.78032$ |
|------------------|------------------------------|-------------------|
| $m_2b = 3.858$   | $\log \beta_2{}^2 = 26733$   | $m_2^2 = 59.527$  |
| $m_3b = 7.030$   | $\log \beta_3^2 = 3.1946$    | $m_3^2 = 197.672$ |
| $m_4 b = 10.183$ | $\log \beta_4{}^2 = 3.5164$  | $m_4^2 = 414.798$ |
| $m_5 b = 13.331$ | $\log \beta_5{}^2 = 3.7504$  | $m_5^2 = 710.884$ |

A mere inspection of these values shows that the value of  $\phi$  can be computed with an accuracy much more than sufficient for any practical purpose from the first two terms of the series (85), if t is as great as  $\frac{1}{100}$ th of a second, and from the first term alone if t is as great as  $\frac{1}{40}$ th of a second. Let  $\phi_0$  represent the first term of (85), then

$$\phi_0 = \frac{400 \pi H_0 e^{-6.1768t}}{(0.78032)(0.20508)},$$

$$\frac{400}{(0.78032)(0.20508)} = 2499.55,$$
(88)

but

which differs from 2500 by about  $\frac{1}{50}$ th of one per cent only.

If there were no eddy currents in the iron, the total induction flux through the rods which make up the core would be

$$\phi' = \pi \mu a^2 H'_{S},\tag{89}$$

and if C' were the strength of the current in the exciting coil at the time t, we should have

$$\pi \mu a^2 N \cdot \frac{dH'_s}{dt} = -w \cdot C' = \frac{-w \cdot H'_s}{4\pi N} \tag{90}$$

and

$$H'_{s} = H_{0} e^{-ht},$$
 (91)

where

$$h = w/4 \,\pi^2 N^2 a^2 \mu = 6.332573 \,+$$

and

$$\phi' = \pi \mu a^2 H_0 e^{-ht}. \tag{92}$$

In the case under consideration we should have very nearly

$$\phi' = 2500 \,\pi H_0 \,e^{-6.332573t} \tag{93}$$

$$4 \pi NC' = H'_{\bullet} = H_0 e^{-6.332573t}. \tag{94}$$

When there are eddy currents the value of  $H_s$  is given with sufficient accuracy by the first term of (83) very soon after the electromotive force has been shunted out of the circuit, that is by the equation,

$$H_s = \frac{2000}{2051} \cdot H_0 e^{-6.1768t} \tag{95}$$

and the ratio of  $\phi$  to  $\pi b^2 n^2 \mu H_s$  is practically equal to the constant 2051/2000, for it is easy to find a very convergent geometrical series every term of which is greater than the corresponding term of the series which begins with the second term of (85), and the sum of this geometrical series is extremely small except for very small values of t.

According to this analysis, the current in the solenoid will have fallen in the first second to the fraction 0.002025 or to the fraction 0.001777 of its original value according as there are or are not eddy currents in the iron.

If the ten centimeter square iron core of the solenoid were built up of straight rods only one millimeter in diameter, we should have b = 1/20, n = 100, and  $\lambda = 1/1000$ ; the *m's* would need to be roots of the equation

$$J_0(mb) = 1000 \, mb \cdot J_1(mb). \tag{96}$$

By using differences of the third order it is possible to show from Meissel's table that the first root is approximately equal to 0.044715 + and the second to 3.83. For the first, then,  $\lambda^2 + m^2b^2 = 0.002000$ , and  $\beta^2 = 6.33077$ . For the second root,  $\beta^2 = 46500$ , and the second terms of the series (83) and (85) become negligible almost immediately after the electromotive force has been removed from the circuit.

In this case

$$\phi_0 = 2500 \,\pi H_0 \cdot e^{-6.33077t} \tag{97}$$

very nearly; and

$$\frac{C}{4\pi N} = H_s = H_0 \cdot e^{-6.33077t} \,, \tag{98}$$

so that the disturbing effects of the eddy currents are comparatively slight. At the end of one second, the current will have fallen to the fraction 0.001777 of its original value or to the fraction 0.001781, according as eddy currents were absent or existent. These differ by only about one two hundred and fifty thousandth part of the original current strength. We may note in passing that a very approximate value (correct to four significant figures) of the first root of the equation might be found by equating to unity the coefficient of the first term of the series (83).

If the core of the solenoid were made of wire one tenth of a millimeter in diameter, such as is now in common use in coils intended for loading long telephone circuits, we should have b = 1/200, n = 1000,  $\lambda = 1/100000$ , and m would need to satisfy the equation

$$J_0(mb) = 100000 \ mb \cdot J_1(mb). \tag{99}$$

It is easy to see that the first root of this has a value very nearly equal to 0.0044721, and that the effects of eddy currents would be quite inappreciable.

Having considered somewhat at length — on the supposition that the induction flux in the air spaces of the core might be neglected — the manner in which a current in the solenoid would decay if the electromotive force were suddenly removed from the circuit without changing the resistance, we may now return to the more general case to which the equations (74) and (76) belong, and remark that in the ideal case where eddy currents are supposed to be absent (68) takes the form

$$H'_{s} + \frac{4\pi N^{2}}{w} (21.46) \frac{dH'_{s}}{dt} + \frac{4\pi \mu N^{2} n^{2} \pi h^{2}}{w} \cdot \frac{dH_{s}}{dt} = 0, \quad (100)$$

whence 
$$H'_{s} = H_{0} \cdot e^{-6.31567t}$$
. (101)

It is clear at the outset that the larger roots, at least, of the two equations (76) and (79) will be very different, since the second member of (76) soon has a negative coefficient. If then the coefficients of the series (77) could be found, the series (74) and (83) would not resemble each other in appearance for large values of b and small values of the time. If, however, b is fairly small, as it usually is in practice, we may dismiss all thought of the infinite series, since it is easy to choose the coefficients of two or three terms of the form (73) so that the initial condition shall be satisfied very approximately. In many cases one term suffices.

Let us consider first the case — already treated in another way — of a square core of 100 square centimeters cross-section, built up of long straight wires 1 millimeter in diameter; so that b = 1/20, n = 100,  $l\beta^2 = 1.36620 \ m^2b^2$ ,  $kn^2 = 1000$ , and the equation for mb has the form

$$J_0(x) = \frac{1000 x}{1 - 1.36620 x^2} J_1(x). \tag{102}$$

It is possible to show by a rather long application of the method of trial and error, using third differences in Meissel's table, that the value of the first root is 0.044654+ and this corresponds to m = 0.89308,  $\beta^2 = 6.31351$ ,  $J_0(mb) = 0.9994891+$ .

If, then, we consider the single term

$$Q = H_0 e^{-6.31351t} \cdot J_0(0.89308 r), \tag{103}$$

Q will satisfy (70) and will vanish when t is infinite. When t is zero, Q will be equal to  $H_0$  for r=0, and will differ from  $H_0$  by about one twentieth of one per cent when r=b. The second root of (102) is roughly equal to 3.8 and the corresponding value of  $\beta^2$  is about 45,000, so that the exponential factor would soon be very small. An inspection of the graph of  $J_0(x)$  shows that if we were to use several terms of the form  $L \cdot e^{-\beta^{2t}} \cdot J_0(mr)$ , we could easily form a function which should differ very little from  $H_0$  for any value of r up to b, when t was zero; but it is clear that after the lapse of about 1/5000th of a second, all the terms beyond the first would be negligible, and there is no practical advantage in using more than one term.

We may assume then that the value of H in any one of the iron rods is given fairly accurately, except at the very beginning, by (103). Since  $4\pi NC = H_S$  the current in the solenoid falls in the first second to 0.001808 of its original value, or to 0.001812 times that value according as eddy currents are absent or present. These fractions differ from each other by about one two hundred and fifty thousandth part of the original current strength. Another close approximation to the value of H may be made by dividing (103) by  $J_0$  (mb) and another by multiplying the second member of (103) by

$$\frac{1+J_0(mb)}{2J_0(mb)}. (104)$$

These changes would not affect the relative rate of decay of the current.

The nearness of the approximation to the value of the field attainable by a single term is evidently much increased as the diameter of the iron wire of which the core is built up is decreased. If as before a=5, but if b=1/200, n=1000, the value of the first root of the equation for mb will be 0.00446616, nearly, and the value of  $J_0(mr)$  will not change by so much as 1/1000000th part of itself as r changes from 0 to b. A single term, therefore, will represent H with great accuracy. In this case the effect of eddy currents is wholly inappre-

ciable. Of course this statement does not apply to the case of an alternate current of very great frequency.

In the problem just considered the electromotive force was suddenly shunted out of the solenoid circuit after a steady current had been established in it, and, on the assumption that the permeability of the iron was fixed, the value of the magnetic field within the core was determined as a function  $[H_0, f(t, r)]$  of the time and the space coordinates. The function f satisfies (65) and (68), vanishes when t is infinite, and is initially equal to unity. If the solenoid circuit containing an applied electromotive force E be suddenly closed at the time t = 0, and if the ultimate value  $(4\pi NE/w)$  of the magnetic field in the core be denoted by  $H_{\infty}$ , the value of the field at any time will be given by the equation

$$H = H_{\infty} [1 - f(t,r)]. \tag{105}$$

The function defined by this equation vanishes, when t = 0, for all values of r, and when t is infinite is equal to  $H_{\infty}$ . It satisfies at all times the equation (65) and the surface equation

$$H_{s} + \frac{4\pi N^{2}}{w} (A - n^{2}B) \frac{dH_{s}}{dt} + \frac{4\pi\mu N^{2}}{w} \int \int \frac{\partial H}{\partial t} dx \, dy = \frac{4\pi N}{w} \cdot E, \quad (106)$$

and such a function is evidently unique.

Although in practice the permeability is not fixed, the analysis of this section enables us to shut in between narrow limits the effects of eddy currents in many cases, and to assert, when this is the truth, that in a given instance the effects of such currents will be negligible, if the pieces of which the core is built are properly varnished.

It is sometimes possible to get interesting information about the magnetic properties of the core of a transformer which has several coils, and about the excellence of the insulation of the sheets of which it is made, by observing the sudden changes in the currents in the coils when the inductances of the system are impulsively changed, or by studying the rate of propagation of the induction flux into the core, but these subjects must be left for the next instalment of this paper.

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# THE DEMAGNETIZING FACTORS FOR CYLINDRICAL IRON RODS.

BY C. L. B. SHUDDEMAGEN.



## THE DEMAGNETIZING FACTORS FOR CYLINDRICAL IRON RODS.

BY C. L. B. SHUDDEMAGEN.

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### OUTLINE OF THE SUBJECT.

It has long been known that when an unmagnetized iron bar is placed in a fixed magnetic field H' and thereby becomes magnetized, the actual force H within the iron is not so great as the original permanent magnetic force at the same point before the iron was introduced. The vector difference  $H_{i}$ , between the original force and the actual force resulting after the iron is brought in, is called the "demagnetizing force" due to the magnetism which has been induced in the iron. original uniform field does not in general induce a uniform demagnetizing field within a piece of iron; in fact, it is commonly accepted that there is only one practical exceptional case: an iron ellipsoid placed so that a given one of its axes is parallel to the direction of the original uniform field. In this case the demagnetizing force for a given ellipsoid with a given axis parallel to the field is simply proportional to the resulting uniform intensity of magnetization I; and the proportionalityfactor N is found by theory to depend only on the dimensions of the ellipsoid, that is on the semi-axes a, b, and c. Moreover, when the ellipsoid is a body of revolution, so that b = c, then we have a simple formula expressing N as depending solely on the value of the ratio a/b. This N is commonly called the "demagnetizing factor" for the ellipsoid.

Lord Rayleigh <sup>1</sup> first pointed out how from a knowledge of N a hysteresis curve obtained for an iron ellipsoid of revolution and plotted on the B vs. H' plane, could be "sheared back" into the limiting hysteresis curve for an ellipsoid of the same cross-section, which would be approached as the length of the axis which lies parallel to the field grows longer and longer. The same process is evidently applicable to a simple magnetization curve obtained by letting the applied field H'

range from 0 to its maximum value, increasing continuously, and the iron being initially unmagnetized. The curve obtained by backshearing is called the "normal" curve of magnetization for the kind of iron used. As the applied field H' is now the same as the resulting field H, the demagnetizing field having disappeared, this normal curve gives us the true permeability  $\mu$  and susceptibility  $\kappa$  for every H, and is therefore the characteristic curve of the iron which we must use in order to get correct values for the physical quantities mentioned. Ewing and other investigators have made much use of this backshearing process in working out hysteresis curves obtained for long iron wires, it being assumed, while experimental determinations were still lacking, that cylindrical iron wires could be regarded as behaving magnetically like ellipsoids of the same length and cross-section, provided the ratio of length to diameter was not too small.

The first attempt to find numerical values for the demagnetizing effect in cylindrical iron rods was made in 1894 by Du Bois  $^2$  in discussing the only magnetization curves with varying length of rods which had up to that time been published: six by Ewing, obtained ballistically,  $^3$  and a few by Tanakadaté, taken by a magnetometric method.  $^4$  From these results Du Bois constructed a table of values for N for values of  $^{11}$  ranging from 10 to 1000, where  $^{11}$  = ratio of length L to the diameter D, of the rod. He evidently considered that N remains practically constant for the whole range of magnetic intensity. Du Bois's values of N for cylinders are from 10 per cent to 20 per cent smaller than for the corresponding ellipsoids, that is ellipsoids having the same ratio of length to maximum cross-section.

In 1895 C. R. Mann published <sup>5</sup> an extended series of results, obtained magnetometrically, for the demagnetizing factors of iron cylinders. The leading points brought out by this investigator, for the rods experimented on, most of which were of small diameter, are: (1) The N's for cylinders are very nearly constant for all intensities of magnetization below I = 800; after this point they increase rapidly as I increases. (2) For the range in which the N's are practically constant, they vary but a very few per cent from the values of the N's for the corresponding ellipsoids. Mann does not believe that ballistic and magnetometric determinations of N will give comparable results.

The most recent work on the demagnetizing factor which I have seen, is embodied in a short but extremely suggestive paper published

<sup>&</sup>lt;sup>2</sup> Magnetische Kreise, Berlin, 1894, pp. 36-45; Wied. Ann., 46, 485-499 (1892).

<sup>&</sup>lt;sup>3</sup> Phil. Trans., 176, II, 535 (1885).

<sup>&</sup>lt;sup>4</sup> Phil. Mag., **26**, 450 (1888).

<sup>&</sup>lt;sup>5</sup> Dissert., Berlin, 1895; Phys. Rev., **3**, 359-369 (1896).

in 1901 by Carl Benedicks.<sup>6</sup> This investigator, while working on the subject of pole-distances in cylindrical rods, interested himself in a few careful experiments on the demagnetizing factors. He gets for a hard steel rod of diameter 0.8 cm. and a length equal to 25 diameters, hysteresis curves by means of both the magnetometric and the ballistic methods. Then by turning it down on the lathe, he transforms the same specimen of iron into an ellipsoid of revolution of length equal to 30 diameters, and gets a hysteresis curve magnetometrically. This last curve is, by means of the known ellipsoid N for m=30, backsheared into the "normal" curve, which, according to Benedicks, can then be used to determine the N for any point on either the ballistic or the magnetometric curve for the cylinder. The result is that the magnetometric N behaves qualitatively exactly like that of Mann, but the ballistic N, after likewise remaining practically constant up to I=800, decreases rapidly as I is further increased.

The present paper is an attempt to contribute to the subject a discussion of the demagnetizing factor for cylinders as determined ballistically. It will appear later that the curve on the B vs. H' plane (or the I vs. H' plane) which determines the back-shearing from a magnetization curve of a finite cylinder to the limiting normal curve, is quite different from the straight line which obtains in the case of the ellipsoid of revolution. It has, in fact, two opposite curvatures: one near the origin, and the other soon after the maximum value of the susceptibility has been passed. The first curvature is not very marked, and it turns out, as has been found before for the magnetometric N, that up to values of B = 10,000 (or I = 800) the ballistic N is not far from constant. The upper part of the curve, however, has a violent turn toward the B-axis (or I-axis) just as has been observed by Benedicks for his short steel cylinder. Theoretical reasons can be given to account in a general qualitative way for these experimental results.

Hitherto it has been the common custom, for lack of experimental evidence on the subject, to regard the N for iron cylinders, leaving out of consideration the variation of this coefficient with the I, as depending only on the ratio  $\mathfrak{m}=L/D$ , and not on the absolute dimensions of the rod. As practically all the previous results have been obtained from experiments on iron cylinders having a diameter of less than 1 mm., that is, mere iron wires, the question has naturally not received any attention. In the present work the writer had at his

<sup>&</sup>lt;sup>6</sup> Bih. Svenska Vet.-Akad. Handlingar, 27, (1), No. 4, 14 pp. (1902); Wied. Ann., 6, 726-761 (1901).

disposal two magnetizing solenoids very much longer than any which have ever been used before, as far as he knows. Thus it was made possible to obtain complete series of magnetization curves, yielding tables of values for N, for a large number of iron rods, ranging in diameter from 0.2381 cm. to 1.905 cms. The results disclose quite a marked dependence of N on the D, the L/D and I being considered constant. In fact the general rule may be stated that the value of N decreases as the diameter of the iron rod increases.

In the work both the "reversal" and the "step-by-step" methods have been used, and the results obtained may be interesting to some who have had occasion to observe the peculiar disagreements in the results given by these two methods. As a rule the N's calculated from reversal curves will be smaller than those obtained from the "step-by-step" method under the same conditions.

#### Introduction.

When a piece of homogeneous isotropic soft iron of any shape is placed in a magnetic field, it will always become magnetized, and the induced magnetism will in general show its existence by changing the original field outside the iron. The only exceptional cases are those in which the iron is "endless," that is, it is in the form of an anchor ring or a rod of infinite length, with the magnetizing solenoid wound directly over the iron. Whenever an apparent magnetic distribution of superficial charge  $\sigma$  and volume charge  $\rho$  is induced by polarization on or in any body of iron, the magnetic field  $H_i$  due to it combines with the magnetizing field H' to give a resultant field H, so that the actual field which determines the intensity of magnetization I is given at every point by the vector equation

$$H = H' + H_i;$$

and  $I = \kappa H$ , where  $\kappa =$  susceptibility of the iron. Outside the iron H will usually be less than H' in some portions of space, and in others it will be greater than H'. But inside the iron H will in general, perhaps always, be less than H'. Thus in the case of a sphere of soft iron placed in a uniform field H', we shall have, from the theory given in most of the text-books on electricity and magnetism, a uniform field of intensity  $H = H' - \frac{4\pi}{3}I$  within the sphere at any point A, while the

Maxwell, II, §§ 437-438; Webster's Electricity and Magnetism, p. 371; Peirce's Newtonian Potential Function, p. 205.

intensity is  $H' - \frac{4\pi}{3}I + 4\pi I$  at the point B just outside the sphere on that line of H' which passes through the centre of the sphere, while at all points C just outside the sphere and lying in a plane passing through the centre of the sphere and perpendicular to the H'-line mentioned, the intensity will be  $H' - \frac{4\pi}{3}I$ . Figure 1, reproduced from Figure 76 on page 373 of Webster's "Theory of Electricity and Magnetism," shows the resultant lines of force in this case. For a ring or an infinite rod of constant cross-section with the magnetizing solenoids properly arranged, we should get  $H_i = 0$ , and H = H'.

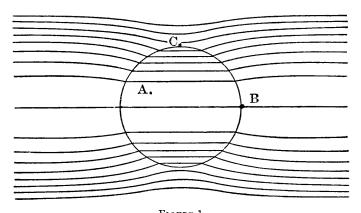


FIGURE 1.

A sphere of permeability 3 in a uniform magnetic field.

At any point in an iron body subjected to a magnetizing field H', the strength of the field  $H_i$  can be regarded as a function of I. If in particular we write the scalar equation

$$H_i = NI$$

and remember that in practical cases the  $H_i$  is a field opposed to H', or tending to demagnetize the iron, then we may speak of the factor N as the "demagnetizing factor" of the particular body of iron at the point considered, with reference to the permanent magnetizing field used, which in all practical cases will be a uniform one. Since  $H_i$  is in general an unknown function of I, therefore N is also some function of I. As the  $H_i$  in the cases to be considered will be directed exactly oppositely to H' in that part of the iron which we shall be interested

in, we shall hereafter use the scalar values for H',  $H_i$ , and I, so that our first equation will become

$$H = H' - H_i = H' - NI.$$

The only case of a magnetized body not endless, in which we can always calculate what the  $H_i$  will be, is where an iron ellipsoid is placed with one of its axes parallel to a uniform magnetizing field H'. If the equation of the ellipsoid is

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1,$$

then it is shown in text-books on the mathematical theory of electricity and magnetism,<sup>8</sup> that if there exists on the ellipsoid a surface distribution of magnetic matter everywhere equal to

$$\sigma = I \cdot \cos(x, n)$$

where I is a constant, and (x, n) is the angle between the positive direction of the x-axis and the exterior normal to the ellipsoid, the volume density  $\rho$  being zero throughout the ellipsoid, then the magnetic field due to this distribution is constant at every point within the ellipsoid and equal to

$$H_i = 2 \pi abc I K_0,$$

where

$$K_0 = \int_0^\infty \frac{ds}{(s+a)^{\frac{3}{2}}(s+b)^{\frac{1}{2}}(s+c)^{\frac{1}{2}}}.$$

This field  $H_i$  is directed parallel to the negative direction of the x-axis, and tends to demagnetize the iron; we see furthermore that it is directly proportional to I. The constant I is simply the intensity of magnetization, uniform within the ellipsoid. To keep this magnetic distribution in equilibrium it is sufficient if we apply a uniform magnetic field parallel to the positive x-axis, of such a strength H', that when diminished by the demagnetizing field  $H_i$ , there will remain in the ellipsoid the uniform resultant field  $H = I/\kappa$ , where  $\kappa$  is the susceptibility corresponding to the magnetization I, for the kind of iron under consideration. Of course if the  $\sigma$  has initially been chosen greater than the maximum value of magnetic intensity attainable, it will be

<sup>8</sup> Maxwell, II, §§ 437 and 438: Webster, Elec. and Mag., §§ 192, 196; Peirce, Newtonian Potential Function. § 69.

impossible to realize such a distribution. If we have a possible case, then

$$H = H' - H_i = H' - 2 \pi abc \cdot K_0 \cdot I.$$

Now the factor  $2\pi abc \cdot K_0$  is constant for a given ellipsoid, and is called its "demagnetizing factor" N. When the iron is an ellipsoid of revolution (b=c), we can integrate  $K_0$  and get a simple formula for N as a function of a/b, the ratio of the length of the ellipsoid to its greatest diameter.<sup>9</sup> It is, when written in terms of  $\mathfrak{m}$ ,

$$N = \frac{2 \, \pi \mathrm{m}}{(\mathrm{m}^2 - 1)^{\frac{3}{2}}} \log \left( 2 \, \mathrm{m} \sqrt{\mathrm{m}^2 - 1} + 2 \, \mathrm{m}^2 - 1 \right) - \frac{4 \, \pi}{\mathrm{m}^2 - 1}$$

When 1 is negligible in comparison with m<sup>2</sup> the formula assumes the simple form

$$N = \frac{4\pi}{m^2} (\log 2 \, \mathfrak{m} - 1).$$

This N does not depend, therefore, on the softness of the iron nor on the magnetizing field, provided the iron ellipsoid was initially demagnetized and our magnetizing field has been continuously increased from zero to its final value.

If the iron is perfectly "soft," or incapable of retaining magnetism when the magnetizing force H' is withdrawn, then any field H' will produce a unique magnetization. The uniform H' along the major axis of the ellipsoid of revolution will therefore produce such a magnetization as we found would be kept in equilibrium by the same H'. As the iron we deal with in practice is not "soft," but shows hysteresis, we find it necessary to define susceptibility as the ratio of I/H when the iron is slowly carried from zero magnetization to the value I, the magnetizing field to increase slowly and continuously up to the proper value H'. Under these conditions it is reasonable to suppose that any magnetizing field will give a unique magnetic distribution, and our results hold true.

Suppose we desire to measure the susceptibility of a specimen of iron in accordance with our ideal definition, so that it may be free from ambiguity; let us consider the suitability for this purpose of the various experimental methods now in use. The fluxmeter is an instrument recently invented, which attempts to give permanent deflections which are proportional to the changes of magnetic induction through a secondary circuit, and these deflections are independent of the time-

<sup>9</sup> Maxwell, II, §§ 437-438.

intervals in which these changes complete themselves. The performance of this instrument is as yet far from satisfactory. If it could be made perfect, we should have an ideal method for permeability determinations, for we could then increase the magnetizing field as slowly as we please, reading off the corresponding magnetic inductions for any desired values of the field. It is probable that the oscillograph methods are at present much more to be preferred, as they can be made to record accurately the slow and long-continued changes of magnetic induction through large masses of iron.

A very good method to use is the "step-by-step" magnetization, where ballistic throws are produced in a Thomson galvanometer, or in a D'Arsonval galvanometer when we use proper precautions to secure the proportionality of throws to the flux changes. These changes in magnetic induction through a secondary coil wound around the iron specimen to be tested are most conveniently obtained by sudden decreases (or increases) in the resistance of the primary circuit, consisting usually of a storage battery and the magnetizing solenoid. arrangement it is not difficult to obtain cyclic hysteresis curves. It has been shown 10 that the maximal induction B (or I) which is reached varies with the number of steps taken, the difference being most marked in the region of greatest permeability. As the number of steps is increased continually in different experiments, the B vs. H curves move nearer the H'-axis, but soon approach the limiting curve for a slow continuous change of H', which, as we saw before, is the one curve that, after the proper back-shearing, will give values for the permeability (and susceptibility) conformable to the ideal definition. Lastly in order of accordance with the ideal definition of susceptibility comes the "reversal" method of measuring ballistic induction throws, which is entirely contrary to a slow magnetization, but which is often the most convenient of all the methods to use, and which gives the most self-consistent determinations; that is, repeated magnetizations will give almost identical results. Both the "step-bystep" and the "reversal" methods of measuring magnetic induction may give results depending on the particular experimental conditions employed, unless one takes proper precautions. Thus the time-constant L/R of the primary circuit should be only one or two per cent of the time it takes the galvanometer-needle to reach its greatest deflection, which time will be the quarter-period of the needle suspension system. It should be noted that when there is a great bulk of iron in the mag-

<sup>&</sup>lt;sup>10</sup> F. Rücker, Diss. Halle, 1905, 106 pp. 20 plates; Elektr. ZS. 26, 904-905, 979 (1905).

netizing solenoid, the L may be enormously large. There are two ways of realizing the condition of the smallness of the time-constant as compared with the quarter-period: (1) We may use a storage battery of high E.M.F. in the primary circuit, which will necessitate large R's in the circuit in order to give magnetizing fields of the desired intensity; (2) It is quite possible to increase the moment of inertia of the needlesuspension so as to give a complete period of several minutes. Several of the experimental series obtained in this investigation by means of the reversal and step methods illustrate very forcibly how these two different methods may lead to various determinations of the susceptibility. Finally, the magnetometric methods are often very useful. especially in accurate determinations of magnetic moment of short iron magnets. With none of these magnetometric methods can we measure the I at any particular part of the iron bar, but get instead a mean value of I (moment/volume of bar) for the whole rod. Plotting I vs. II' curves for various lengths of soft iron cylinders, we can find mean demagnetizing factors N, by means of which a "normal" curve can be constructed. But it will be seen, after a little reflection, that the curve Mean I vs. Mean H which we get here is not necessarily the same, or even approximately the same, as the "normal" curve of I vs. H, which gives corresponding values of I and H in the middle of the bar immediately surrounded by the secondary coil, and which may be regarded as an extremely close approximation to the I and H at a single point in the iron. It is this fact which accounts for the wide difference which has been found between the N as determined ballistically and the N as determined magnetometrically. It is hardly likely that the process of back-shearing a magnetometric magnetization curve will yield a curve from which anything like the true susceptibilty can be found.

Returning now to our iron ellipsoids of revolution, we see that if we know the ratio of the length to the diameter of one of them, we can calculate exactly what the demagnetizing factor N will be. Ewing and Du Bois, in their texts on magnetism, give tables of values of N (see page 204) for various ratios a/b. It follows from a paper by Lord Rayleigh, 11 that if we magnetize any iron ellipsoid of revolution having a known ratio a/b, from zero magnetism to full saturation, measuring the I ballistically by means of a small secondary coil around the middle part of the rod, and plot out the curve I vs. H', we can "back-shear" this curve parallel to the H'-axis by the amount  $H_i = \Delta H = NI$ , and thus construct the "normal magnetization" curve, for which H = H', and from which alone the true susceptibility can be found for every I.

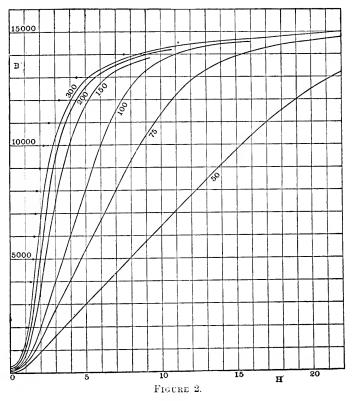
<sup>&</sup>lt;sup>11</sup> Phil. Mag., **22**, 175–183 (1886).

Suppose now that we have any elongated piece of iron with a secondary coil wound around it near the middle and connecting with the terminals of a ballistic galvanometer. Suppose also that the normal magnetization curve for the kind of iron used were known, say, by taking measurements ballistically on an anchor-ring made of the same material. (As a matter of fact this method does not apply, for by welding the ends of a rod together to form a ring, we change the magnetic behavior of the iron unavoidably, to say nothing of differences which exist in two different specimens of iron made from the same kind of iron.) If we now find experimentally the actual magnetization curve, and plot it together with the normal curve on the I vs. H' plane, and plot on a similar plane, which we shall call the I vs. (H'-H) or the I vs.  $H_i$  plane, the differences of the abscissae (which are  $\Delta H = H_i = NI$ ) of the two curves for each I, against this same I, we shall call this last curve the "N-curve" for the particular piece of iron and the particular position of the secondary coil, it being understood that we have placed the iron in a definite position in a given magnetic field, or distribution The I of the actual magnetization curve is the average I existing in the volume of iron immediately surrounded by the windings of the coil. In general we do not know what the form of the N-curve may turn out to be, until we obtain it experimentally; in the ellipsoid of revolution placed with its major axis parallel to the uniform field, this N-curve will, according to theory, obviously be a straight line through the origin and making with the I-axis the angle whose tangent is equal to  $N \cdot (\text{ratio of } H' \text{ scale unit to } I \text{ scale unit}).$ 

Now since ellipsoids of revolution are not very easily constructed, the case most important for magnetic measurements in laboratory practice is that of the cylindrical iron rod with ends squared off, and the secondary coil wound around just in the middle part of the rod, a uniform magnetizing field, such as can be secured inside a long solenoid, being used to produce the H'. Here we do not obtain a uniform I by placing the rod in a uniform field, and although the problem is determinate rnathematically, no one has as yet succeeded in obtaining the solution. The great difficulty lies in the fact that the susceptibility is not constant throughout the rod for any given H'. The lines of magnetization run parallel only through the middle cross-section of the rod, where the secondary coil is wound. If, then, we wish to know the N-curves for some kind of iron in the form of cylindrical rods, our only resource is to find experimentally a series of I vs. H' curves for greater and greater values of  $\mathfrak{m} = L/D$ , where L = length, and  $D = \frac{L}{D}$ diameter of the rod. Then we must find, by some extrapolation method, or otherwise, the limiting curve as ut becomes larger and

larger. We may then plot out the abscissa-differences between this normal curve and all the others, and thus actually construct the Ncurves.

The only experimental magnetization curves for a number of varying m's which had been published before 1895 are those obtained by



Ewing's magnetization curves for a soft iron wire of diameter 0.158 cm.

Ewing  $^{12}$  for m = 50, 75, 100, 150, 200, and 300 (see Figure 2), and some by Tanakadaté for rather small values of m, his highest being about m = 39. Ewing's iron cylinder was a wire of diameter = 0.158 cm. and original length = 47.5 cms., the other m's being obtained by cutting off pieces from each end. The maximum permeability for this iron was found to be  $\mu = 3500$ . Tanakadaté's iron wires were of

<sup>12</sup> Phil. Trans., 176, II, 535 (1885).

diameter = 0.153 cm., the length varying from 2 to 6 cms., also of diameter = 0.115 cm. and a length originally 33.4 cms. For the shorter specimens he used Gauss's A position, that is, the rod is placed east and west and the magnetometer is placed in the prolongation of the rod's axis; for the longer wires Ewing's method was used, in which the solenoid and wire are placed vertically, with an extra solenoid to compensate for the earth's field, and the magnetometer being placed east or west of one end of the wire.

Du Bois subjected these data to a very extensive discussion. He developed the proposition that, provided the length of the rod is sufficiently great compared with its diameter, then  $N \mathfrak{m}^2 = \text{constant}$ . This constant he finds from Ewing's curves to be equal to 45, provided m ≥ 100. The reason why this formula cannot possibly hold for short rods is that the theory of Du Bois assumes that the average magnetization intensity I in the whole rod differs but very little from the I within the secondary coil in the middle of the rod; in other words, that the magnetization is practically uniform. Of course this is never realized for finite rods and ordinary fields H', but it seems at first sight as if the magnetization in a rod of large m should be fairly uniform. If we follow Du Bois's method, which gave him the necessary data to construct his table of values for N in case of cylinders, we may measure abscissa-differences, which are proportional to N, for the curves for rods of large m's, and form three or four simultaneous equations, each of which linearly contains x, the abscissa-difference of the normal curve and the I vs. H' curve for the largest m used in the equations. Any two of these equations give x, and we can thus construct the normal curve, which gives us immediately all the N-curves by plotting abscissa-differences as before. Du Bois, from the meagre data at his command, found values for N for various m's and has collected the results in tabular form (see table, page 204) in his book "Die Magnetischen Kreise in Theorie und Praxis" ("The Magnetic Circuit in Theory and Practice," translated by Atkinson). He apparently considers the N-curves to straight lines, as far as practical purposes are concerned, that is N is not a function of H (or I); at any rate he does not mention any such variation of N. And as to the question whether or not the N for a given m and I varies with the diameter of the rod, no data were at hand.

Now there is no reason to believe the N-curves for cylindrical rods of the same diameter to be straight lines; and since we know that the building up of magnetization, and perhaps even the final result, is very decidedly modified by the bulk of iron magnetized, it is quite likely that thick massive rods of iron really give different values for N from

those calculated by Du Bois for the "iron wires" used by Ewing and Tanakadaté. And, lastly, it is quite possible that the N may vary with the degree of softness and other physical characteristics of the iron magnetized. The present investigation was therefore undertaken to test as accurately as possible the true nature of the N-curves, whether they are really straight lines or not, and their possible variation with the diameter of the rod. Moreover, a table of values of N determined carefully by the ballistic method for thicker rods than has been done so far, would be quite useful in the practice of electrical engineering as, for instance, in the designing of dynamo machinery.

Before discussing the experimental results let us consider theoretically the N-curves for a given kind of iron and a given diameter, the length alone being varied. We shall attempt to show that this backshearing curve has two opposite curvatures. Let us suppose that we know the normal magnetization curve of our iron. We want to learn something about the nature of the N-curve for a cylindrical rod of homogeneous isotropic iron whose length is finite but otherwise arbitrary. All the facts which we need are these: (1) The I has a maximum value  $I_{\infty}$ , which is reached asymptotically by increasing the magnetizing force H' indefinitely. (2) In any finite cylindrical iron rod, no matter how short, the lines of magnetization can apparently be made straight, or I made uniform, by applying an infinite H'. And whenever I/H, the susceptibility, has rather small values, then the condition of uniform I is with some approximation realized. (3) Although the normal curve and all other I vs. H' curves for rods of finite length do not run into the origin tangential to the H'-axis, they do make a very small angle with it. In other words, the susceptibility approaches a small value  $\kappa = 15$ , or thereabouts, as the H' decreases indefinitely. 13 (4) The normal curve has one, and only one, point of inflection.

With regard to the second part of (2) it might be noted that the non-uniformity of I in an iron cylinder placed parallel to the lines in a uniform magnetic field is measured in a rough way by the largeness of the ratio  $H_i/H$ , the demagnetizing force divided by the resulting force, at the point considered. Now  $H_i = NI = N\kappa H$ , so that this ratio is merely  $N\kappa$ . Therefore, if we suppose for the moment that N for a given finite rod is nearly constant for a considerable range of I, it follows that the magnetization will be the nearer to uniformity the smaller the susceptibility is.

Let us then consider the N-curve for a rod for which  $\mathfrak{m}=\mathfrak{m}_1$ , say.

<sup>&</sup>lt;sup>13</sup> C. Baur, Wied. Ann., **11**, 399 (1880). Lord Rayleigh, Phil. Mag., (5), **23**, 225–245 (1887).

In Figure 3 let P and Q be two points on the I vs. H' curve for  $\mathfrak{m}_1$ , where Q has the ordinate of the point of inflection  $Q_0$ , and P is any other point of the magnetization curve. Now suppose the rod were magnetized by an infinite H' to the maximum  $I_{\infty}$ , so that all the  $\pi a^2 I_{\infty}$  lines are straight and enter and leave the rod at the squared-off ends (a being the radius of the rod). In this case the distribution of magnetism which we may consider the cause of the demagnetizing force  $H_i$ , or  $\Delta H$ , is wholly superficial, and as far away from the secondary coil, where I is measured, as possible, and it has a perfectly definite value  $\Delta H_{\infty}$ , say, which we lay off on the I vs. (H'-H) plane, getting the point K, and we draw the line OK. We see now that if, as we in-

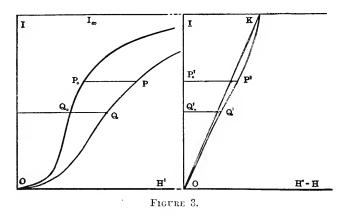


Diagram illustrating magnetization and back-shearing curves.

crease I from zero to  $I_{\infty}$  by continually increasing H', the lines of magnetization were always straight, then the demagnetizing force would always be proportional to I, no matter what the susceptibility might be, and the N-curve would be the straight line OK. Another case where the N-curve would be a straight line  $OK_1$  would be realized if the susceptibility were a constant for all values of I from O to  $I_{\infty}$ . In this case no volume density would appear by magnetization, and any two fields  $H_1'$  and  $H_2'$ , giving separately the surface densities of magnetism  $\sigma_1$  and  $\sigma_2$ , could be superposed, so that a magnetizing field  $H_1' + H_2'$  would give the superficial distribution  $\sigma_1 + \sigma_2$ . This last supposition would result in there being no limit to the intensity of magnetization. As a matter of fact the I is uniform only for an infinite H'. At the point P, if P is not the origin, more or less lines of induction will leave

the iron rod along the curved surface, as is well known. Now from the mathematical theory we know that in the case of "soft" iron B, or  $\mu H$ , is a solenoidal vector, continuous throughout all space, whether iron or air, not containing any fixed magnetic charges. Wherever lines of induction leave the surface of the iron we must therefore have positive  $\sigma$ ; for the vectors H and I, although not solenoidal in the iron, have always the same distribution as the vector B, I is zero outside the iron, and  $\sigma = I \cdot \cos(n, I)$ . This means that a part of the surface distribution  $\sigma$  of the magnetism is closer to the middle of the rod than it would be if I were uniform. There is also some magnetic matter in the form of volume distribution  $\rho$ . This, however, does not materially influence the argument, although it complicates matters somewhat. We shall come back to the volume charge later. Therefore, as far as the surface magnetism is concerned, the demagnetizing force  $\Delta H_P$  is for every point P actually greater than it would be if I were uniform. We thus reach the result that the N-curve has the end-points O and K, but lies everywhere else to the right of the straight line OK. Indeed for the most part the N-curve will be very decidedly to the right, for a very large number of the lines of induction will leave the iron rod before reaching the ends of the rod. The demagnetizing factor  $N_{\infty}$  is the minimum value of N, although  $\Delta H_{\infty}$  is by no means vanishingly small. Near the origin the ratio of H to I is comparatively large, although of course still a fraction, so that according to (2) the I is more nearly uniform than for higher points on the curve, so long as we do not pass the point of maximum susceptibility, which is the point of tangency of a line drawn from the origin to the normal magnetization curve; therefore the N-curve is more nearly tangent to the line OK at the origin than for points a little more removed. As we increase H' from O to some point Q whose I is of the order of I at  $Q_0$ , the lines of magnetization increase continually, but a larger and larger fraction of lines leave the rod before reaching the ends, and N increases continually. Again, as we follow the magnetization curve from any very large but finite value of H' down toward Q, the I-lines spread out in greater and greater proportion, and the N increases for quite a long interval. This shows that the curvature of the N-curve changes sign at some point  $Q_1$ , which is a point of inflection for the N-curve, and probably the only one. We should expect, therefore, that the curve drawn in the second part of Figure 3 on the I vs. NI plane represents roughly the qualitative behavior of an N-curve for a finite rod.

It remains to be shown that the volume distribution does not invalidate the argument just given. From the theory of magnetism we know that this can be expressed in the form

$$\rho = \frac{h_{\kappa}h_{\tau} \cdot \cos\left(h_{\kappa,h_{\tau}}\right)}{\mu},$$

where  $\mu =$  the permeability,  $h_{\kappa}$  and  $h_{\tau}$  the gradients of the susceptibility and resultant magnetic potential function, respectively, and  $(h_{\kappa}, h_{\tau})$  is the angle made by the directions in which  $\kappa$  and V increase most rapidly. For we have by Poisson's Equation,

$$\nabla^2 V = -4 \pi \rho,$$

and from the fundamental equation of magnetic polarization,

$$\begin{split} \rho &= - \text{ Divergence } I = - \left[ \frac{\partial}{\partial x} (\kappa X) + \frac{\partial}{\partial y} (\kappa Y) + \frac{\partial}{\partial z} (\kappa Z) \right] \\ &= \frac{\partial}{\partial x} \left( \kappa \frac{\partial Y}{\partial x} \right) + \frac{\partial}{\partial y} \left( \kappa \frac{\partial Y}{\partial y} \right) + \frac{\partial}{\partial z} \left( \kappa \frac{\partial Y}{\partial z} \right) \\ &= \kappa \cdot \nabla^2 Y + \left[ \frac{\partial \kappa}{\partial x} \cdot \frac{\partial Y}{\partial x} + \frac{\partial \kappa}{\partial y} \cdot \frac{\partial Y}{\partial y} + \frac{\partial \kappa}{\partial z} \cdot \frac{\partial Y}{\partial z} \right] \cdot \end{split}$$

Eliminating the  $\nabla^2 V$  we get the equation above. Now  $h_{\kappa}$ ,  $h_{\tau}$ , and  $\mu$ are all intrinsically positive. The  $h_{\kappa}$  becomes zero under special conditions, and is vanishingly small when the iron becomes fully satur-Therefore the sine of  $\sigma$  is governed by the cos  $(h_{\kappa}, h_{\tau})$  alone. Considering only the half of the iron cylinder on which the positive  $\sigma$ appears, we see that I always increases from the end of the rod toward the centre, while  $\rho$  does so as long as the magnetization at the centre of the rod has not been pushed beyond the maximum susceptibility point. Under these conditions  $(h_{\kappa}, h_{\nu})$  is an acute angle, and therefore  $\rho$  is positive. Therefore the argument regarding the curvature of the N-curve in the neighborhood of the origin is even strengthened all the more on account of the positive  $\rho$  intensifying the demagnetizing force. Thus the lower curvature is proved (although not quite rigorously, mathematically speaking), and since the N-curve must end in the point K, there must be a curvature in the upper part of the N-curve directed oppositely to the first one.

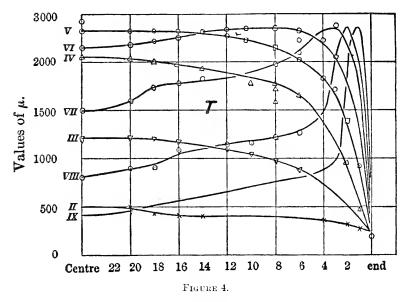
An interesting fact perhaps worth noticing in regard to the volume distribution  $\rho$  of the magnetism is that as soon as the point of maximum susceptibility has been passed over, which will first occur at the centre of the rod, there will appear some negative  $\rho$  near the centre of the rod in that half of the rod which always carries the positive sur-

face distribution. This is due to the fact that  $(h_{\kappa}, h_{\tau})$  now has become an angle of 180° at points in the axis of the rod and near the centre of the rod, while further away from the centre but still along the axis, where the  $\kappa$  has not yet reached its maximum, the angle  $(h_{\kappa}, h_{r})$  is still Somewhere between the two regions will be a curved surface for all points, of which  $\kappa$  has its maximum susceptibility, and  $h_{\kappa}$  is zero, and the angle  $(h_{\kappa}, h_{\tau})$  is discontinuous by  $\pi$ , so that  $\rho$  is everywhere zero on the curved surface, which separates the regions of positive and negative  $\rho$ . As the iron is subjected to higher and higher fields H', this curved surface moves further and further away from the centre, until finally there is only negative  $\rho$  left in that half of the iron rod which has the positive surface magnetism. This occurs just as soon as every point in the iron has been magnetized past the point of maximum  $\kappa$ . The presence of this negative  $\rho$  may perhaps account very largely for the fact that N is not far from constant for quite a long range of I. When saturation of the iron with magnetism is approached more and more, the k becomes nearly constant throughout the rod and continuously approaches zero, so that  $h_{\kappa}$ , and therefore the negative  $\rho$ , are both becoming vanishingly small. C. G. Lamb 14 gives a set of curves, reproduced in Figure 4, showing the variation of  $\mu$  along an iron rod from centre to end for various applied fields, which illustrate the matter with perfect clearness. Of course the  $\mu$ , when found, as Lamb did, by ballistic methods, with a search coil placed at varying distances from the centre, is the mean value of  $\mu$  for the iron surrounded by the search coil, but it shows the variations along the rod very well indeed.

All the N-curves found in the experimental series of the present paper do not deviate to a very great extent from straight lines for values of B less than 10,000 or thereabouts. They show quite definitely the two curvatures which we were led to expect by theoretical considerations. Above this point, however, the N-curves have an ever-increasing tendency to turn to the left, and at last actually do move from right to left, so that finally we have not only the  $H_i/I (= N)$  merely decreasing, but even the  $H_i$  decreasing. At first this was very puzzling, for it would seem natural to suppose that, although N must really decrease when the iron bar shows saturation, just as we were expecting from the theory, as long as more and more lines of magnetic induction are thrown into the rod when as yet unsaturated with magnetism, there is more and more magnetism induced, which ought to increase the demagnetizing field  $H_i$  continuously.

<sup>&</sup>lt;sup>14</sup> Phil. Mag., (5), **48**, 262-271 (1899).

This, however, is not at all the ease, and the actual facts emphasize the fallacy of considering the magnetization in long iron rods, when not completely saturated, as even approximately uniform. As will appear from the results obtained in this investigation, the values of N are not far from being constant below B=10,000, and they are of the order of magnitude as those found by Du Bois from Ewing's curves, although always somewhat smaller. But let us now find what these N-values would be if our various rods were really uniformly magnetized. In other words, let us find the position of K of the straight line



Lamb's curves showing the change in permeability along an iron rod. The distances along bar are given in inches.

OK in Figure 3. Our rod has the length L and diameter D, so that uniform magnetization would mean  $\pi (D/2)^2I$  units of free positive magnetism on one end of the rod and the same number of negative units on the other end. If L is large compared to D, we may regard the demagnetizing field-intensity  $H_i$  (or NI) at the centre of the rod as caused by a single point-pole of strength  $2\pi \left(\frac{D}{2}\right)^2I$  at a distance of L/2 units of length from it. Then

$$H_i = NI = \frac{2\pi \left(\frac{D}{2}\right)^2 I}{\left(\frac{L}{2}\right)^2} = \frac{2\pi I}{\mathfrak{m}^2}.$$

Therefore, for uniform magnetization,

$$Nm^2 = 2\pi = 6 \cdot 28 + .$$

This value for Nm<sup>2</sup>, it will be noticed, is considerably less than the constant 45 as found by Du Bois from experimental data, and which constant led him to construct a table of values for N which, as we shall see later, is probably quite accurate for the iron wires of small diameter used by Ewing and Tanakadaté. Yet the conditions which Du Bois assumed in order that his theory might be applicable are precisely those which we have here assumed. For the shorter rods Nm<sup>2</sup> would be smaller yet, for the two reasons that the magnetism  $\sigma$  (or I) on the squared-off ends of the cylinder must now be considered further off than the distance L/2, and much of it acts at a small angle; of course the resultant  $H_{ij}$ , which is now really given by a double integral, is directed along the axis of the rod. It is now clear that Figure 3 does not begin to show the tremendous sweep to the left, of the upper portion of the N-curve, which has been found by Benedicks 15 for his rod of steel where m was 25, and which really occurs in every one of the N-curves obtained ballistically.

Let us now compare the values of N for various ellipsoids of revolution, and those obtained by Du Bois for cylindrical rods, with the limiting values of N for uniform magnetization. The values for the shorter rods are calculated from the same formula as the longer ones.

The explanation of the great difference between the actual demagnetizing force under non-saturating fields and the demagnetizing force in case of uniform I is of course found in the fact that in the former case quite a large part of the lines of force leave the curved surface of the iron rod very near the middle of the rod, so that the contributions  $\Delta M/r^2$  to the demagnetizing force count up very heavily in comparison with the magnetism nearer the end of the rod. An ideal uniformly magnetized rod of the same diameter, and having the same number of lines through its middle section as one which is actually magnetized in practice to less than saturation, must be only about  $\sqrt{2\pi/45}$ , or 0.374 times as long, if it is to produce as much demagne-

<sup>15</sup> Bih. Svenska Vet.-Akad. Handlingar., 27, 1, No. 4, 14 pp. (1902); Wied. Ann., 6, 726-751 (1901).

TABLE I.

Demagnetizing Factors. (N.)

| m = L D  | Ellipsoid. | Cylindri | cal Rods.  |
|----------|------------|----------|------------|
| or a, b. | Empsoid.   | Du Bois, | Uniform I. |
| 10       | 0.2549     | 0.2160   | 0 063      |
| 15       | 0.1350     | 0.1206   | 0.028      |
| 20       | 0.0848     | 0.0775   | 0.016      |
| 25       | 0.0579     | 0.0533   | 0.010      |
| 30       | 0.0432     | 0.0393   | 0.0070     |
| 40       | 0.0266     | 0.0238   | 0.0089     |
| 50       | 0.0181     | 0.0162   | 0.0025     |
| 60       | 0.0132     | 0.0118   | 0.0018     |
| 70       | 0.0101     | 0.0089   | 0.0013     |
| 80       | 0.0080     | 0.0069   | 0.00098    |
| 90       | 0.0065     | 0.0055   | 0.00078    |
| 100      | 0.0054     | 0.0045   | 0.00063    |
| 150      | 0.0026     | 0.0020   | 0.00028    |
| 200      | 0.0016     | 0.0011   | 0.000157   |
| 300      | 0.00075    | 0.00050  | 0.000070   |
| 400      | 0.00045    | 0.00028  | 0.000039   |

tizing force at the middle point of the rod as the other suffers. This induced magnetism (both  $\sigma$  and  $\rho$ ) near the centre of a rod of iron magnetized to a value of B somewhat below 10,000, can be readily recognized by its effect on a small compass needle, which will be deflected the moment it is moved a few centimeters from the middle part of the rod toward either end.

It might be of interest to note that the highest possible demagnetizing force would be obtained by placing a very large slab of iron, with plane parallel faces, perpendicular to the lines of an infinite magnetizing field H'; the value of  $H_i$  would be  $4\pi I_{\infty}$ , when the slab is infinite in extent, but has any finite thickness. This  $H_i$  would, moreover, have

the same value at any point whatever in the iron slab. The value of N, the demagnetizing factor, is  $4\pi$  throughout the slab. As in soft iron a negative force of H' less than 10 e.g.s. units of field intensity is sufficient to demagnetize the remanent magnetization which exists in the iron after the original magnetizing field is withdrawn, and the value of  $4\pi I_{\infty}$  is about 200,000 of e.g.s. units, it is easily seen that on removing the infinite field the demagnetizing field  $H_{\epsilon}$  would instantly demagnetize the slab completely.

A diagram of the apparatus and its arrangement, as used practically throughout the present investigation, is shown in Figure 5.

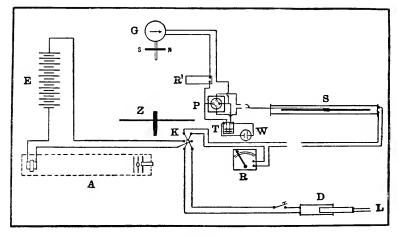


FIGURE 5.

Diagram of apparatus used in the Jefferson Physical Laboratory in obtaining magnetization curves for the present investigation.

## Experimental Methods and Apparatus.

G is a Thomson four-coil ballistic galvanometer with a staticised magnetic suspension, controlled by a permanent magnet S-N, and not shielded at all magnetically, for it was found that when shielded with three large cylindrical iron shells and heavy iron plate tops and bottom, certain unknown magnetic disturbances were caused in these shields, and effectually prevented the needle, which was then non-astatic, from coming to rest. E is the storage battery of from 5 to 20 cells, giving about 2 volts each, for furnishing the current in the primary coil. S is a large solenoid of the following dimensions:

Length = 207.7 cms. Outside diameter = 5.97 cms. Inside diameter = 3.63 cms.

This solenoid was wound on a tube of pasteboard with two wire coils of 3386 turns each, — of No. 18 wire, in six layers, — which were used in parallel, so that

$$H' = 4 \pi n C/10 = 20.5 \cdot (\text{No. of amperes used}).$$

Later on in the work a still longer solenoid was built, in order to experiment on very thick iron rods. A is a "P-3" amperemeter, that is, one of the type so successfully used in the laboratory of the course Physics 3 in Harvard University; it reads with great accuracy up to 1.5 amperes. K is a double reversing knife switch, connected to the solenoid S, and also to a demagnetizing solenoid D, with an iron core in the small coil, which could be connected to the light circuit L. R is a rheostat in series with a system of variable resistance coils, to regulate the current. P is a reversing key to change direction of ballistic throw in the galvanometer. T is a tapping key arrangement with small battery, for bringing the galvanometer magnet needle to Its circuit contains a very high resistance W. Z is the galvanometer scale with telescope, at 116 cms. distance from magnet system. R' is a resistance box in the secondary circuit; by varying this resistance the throws were kept under control, so as to give good accuracy in the readings.

The "P-3" galvanometer was frequently compared with a Weston milliamperemeter with shunt, and the sensitiveness of the galvanometer was often determined during the course of the work by charging a condenser of one microfarad capacity from a battery of four Samson (wet) cells whose voltage was read off on a voltmeter. The sensitiveness, given in centimeter divisions of throw per coulomb, ranged from 1.24 to 1.60. In the latter part of the work the condenser was charged by connecting across a standard resistance of 10 ohms, say, through which about 1 ampere was flowing, thus getting about 10 volts.

In the earlier half of the experiments the "reversal" method was used with great convenience and accuracy in the readings. The magnet suspension does not hold its zero very closely, but is slowly tossed about by magnetic disturbances over a range of 1 mm. scale reading, and sometimes more. Moreover, the zero position, which is quite definite at any one time, often changes slowly during the course

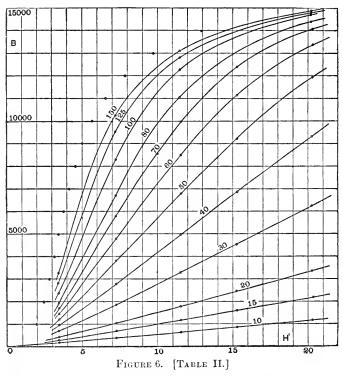
of the day. With the reversal method no attempt to read the zero was made, but instead a number of throws were taken alternately in the plus and minus directions, and then averaged. These throws often agreed regularly to about 1 part in 1000, when taken with a little care. The reversal method, however, has a possible error due to the time-constant of the primary circuit being comparatively large when there is much iron in the solenoid S, and also to the slow establishment of the magnetism in a thick iron rod. This was counterbalanced by making the complete period of the astatic system about 25 seconds, and finally 31 seconds.

The step-by-step method was used only in one series of experiments with the first solenoid S. This method is much harder to carry through successfully, especially since the battery E must maintain its voltage without appreciable drop while furnishing an increasing current for about half an hour, and the zero reading must be taken carefully every little while. Usually several curves were obtained for each length of the iron rod used, so that a good average curve could be constructed. As is well known, the two methods do not give the same magnetization curve, the one by the step method usually, but not always, lying below the reversal method curve.

The iron rods tested in the first solenoid were all of soft Bessemer steel, six feet long and of diameters ranging from 0.2381 cm. (=  $\frac{3}{3.2}$ inch) to 1.270 cms. (=  $\frac{1}{2}$  inch). The secondary coils consisted of from 30 to 400 turns of fine insulated wire wound directly over the middle of the rod. It was found necessary to reverse the magnetism about six times before reading the actual throws, otherwise the readings come out too low. After sufficient data had been collected to construct a curve, equal lengths of the rod were cut off from each end, so as to reduce in from one value to the next. The ends of the rod were then filed smooth and plane. Then a curve was obtained for the shortened length of the rod.

After proper reduction of the observations, the magnetization curves B vs. H' were carefully constructed for all the m's used, on a large sheet of millimeter paper of the dimensions  $43 \times 53$  cms.

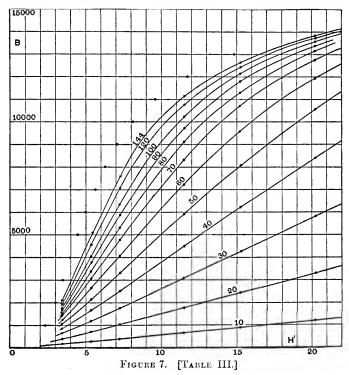
The next problem was to devise some means of getting at the normal curve ( $m = \infty$ ). In the earlier part of the investigation frequent use was made of the principle which leads to Du Bois's experimental formula  $Nm^2 = 45$ , when  $m \ge 100$ . It was found that so long as B did not exceed the value 8000, the formula was fairly well satisfied for m  $\geq$  150, provided only one system of simultaneous equations was used. That is, supposing we had plotted out the actual magnetization curves for m = 300, 250, 200, and 150. If we take all these into account, reckoning therefore the distance in any units of length, say millimeters, from the normal curve to the one for  $\mathfrak{m}=300$  as our unknown x, we shall find the whole set of equations giving a good average value for x, and thus we may construct what might be called "the normal curve based on  $\mathfrak{m}=300$ ." Now if we use only the curves for 250 to 150, so that our next x is the unknown distance from normal



Reversal magnetization curves for a Bessemer soft steel rod of diameter 0.6350 cm.

curve to the curve of 250, we shall again find values for x which satisfy all the equations moderately well. But the normal curve thus determined, which is the normal curve based on  $\mathfrak{M}=250$ , will lie slightly to the right of the first one constructed, — at least every case tried gave this result. Similarly, the normal curve based on  $\mathfrak{M}=200$  will lie to the right of the one based on  $\mathfrak{M}=250$ , and so for the one based on  $\mathfrak{M}=250$ . For higher values of B than 8000 the formula fails to hold at

all. It should be noticed that as the iron rods become nearly saturated with magnetism, the magnetization curves bend around and become more and more parallel to the H'-axis, so that a very slight displacement of the curves up or down may result in proportionately large errors in the construction of the N-curves. The only thing to do is



Reversal magnetization curves for a Bessemer soft steel rod of diameter 1.270 cms.

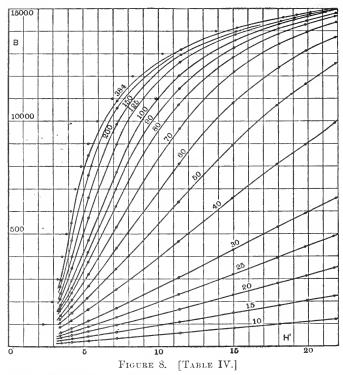
to construct by "trial and error" methods a normal curve which will give the best possible results for the whole body of N-curves.

To be absolutely consistent the N-curves should be constructed from magnetization curves on the I vs. H' plane, for N is defined by H = H' - NI. Substituting in this the value for I from the fundamental equation  $B = H + 4\pi I$ , we get

$$H = H' - N \left( \frac{B - H}{4 \pi} \right).$$

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But as even for the high value H=30, B is somewhere near 15,000, we see that the error introduced by neglecting the H in the brackets is but 1 part in 500, which is much less than the experimental errors. Therefore, since the ballistic throw is proportional to B, it is very



Reversal magnetization curves for a Bessemer soft steel rod of diameter  $0.4763~\mathrm{cm}.$ 

much more convenient to construct the N-curves from the formula

$$H = H' - NB/4 \pi.$$

EXPERIMENTAL RESULTS FOR DEMAGNETIZING FACTORS.

Let us now tabulate the actual values obtained for the end corrections, or demagnetizing factors N, of a number of rods of Bessemer steel (copper coated), which is a very homogeneous soft iron. Later on we shall see just how these values were determined, and give the

necessary data from which the most important table was constructed. It might be noted here that the results for the extremes of magnetization B=1000, and  $B=12{,}000$  are somewhat less reliable, for reasons which will appear. The numbers 10 to 150 are the values of ut used.

TABLE II. [FIGURE 6.]

October 2, 1906.

Diam. = 0.6350 cm. = 1/4 in.

REVERSALS.

| В.    | Values of $N 	imes 10^4$ . |      |     |     |     |     |     |    |    |            |     |     |
|-------|----------------------------|------|-----|-----|-----|-----|-----|----|----|------------|-----|-----|
| В.    | m=10                       | 15   | 20  | 30  | 40  | 50  | 60  | 70 | 80 | 100        | 125 | 150 |
| 1000  | 1990                       | 1010 | 630 | 311 | 199 | 132 |     |    |    |            |     |     |
| 2000  |                            | 1028 | 644 | 328 | 199 | 137 | 104 | 79 | 64 | 41         |     | ٠.  |
| 3000  |                            |      | 653 | 329 | 204 | 137 | 101 | 79 | 62 | <b>4</b> 3 | 30  | 19  |
| 4000  |                            |      |     | 333 | 205 | 138 | 101 | 77 | 60 | 43         | 29  | 19  |
| 5000  |                            |      |     | 333 | 206 | 140 | 102 | 76 | 60 | 42         | 29  | 19  |
| 6000  |                            |      |     | 332 | 206 | 139 | 101 | 76 | 60 | 40         | 28  | 18  |
| 7000  |                            |      |     | 330 | 205 | 139 | 101 | 76 | 60 | 40         | 28  | 18  |
| 8000  |                            |      |     |     | 205 | 139 | 101 | 76 | 58 | 39         | 26  | 17  |
| 9000  |                            |      |     |     | 204 | 139 | 100 | 76 | 57 | 39         | 26  | 17  |
| 10000 |                            |      |     |     | 202 | 137 | 99  | 75 | 56 | 38         | 25  | 17  |
| 11000 | ٠. ا                       |      |     |     |     | 134 | 97  | 73 | 55 | 36         | 24  | 17  |
| 12000 |                            |      |     |     |     | 132 | 95  | 70 | 53 | 34         | 22  | 16  |
| 13000 |                            |      |     |     |     |     | 92  | 68 | 52 | 32         | 21  | 15  |
| 14000 |                            |      |     | ٠.  |     |     | 86  | 63 | 49 | 30         | 21  | 15  |
| 15000 |                            |      |     |     |     |     |     |    |    |            |     |     |

Below each value of  $\mathfrak{m}$  is given the series of values of  $N\cdot 10^4$  obtained, one for each interval of 1000 c. g. s. units of B, or gausses. Of course in all these experiments the column under the highest number  $\mathfrak{m}$  gives values for the first curve obtained, for  $\mathfrak{m}$  is always decreased by each sawing off of the ends of the iron rod.

See Figure 6 for the magnetization curves of October 2, 1906.

The normal curve as determined is indicated in all these figures by the dots spaced every 1000 units of B.

Figure 7 exhibits the curves taken on October 4, 1906, and shown in Table III. It will be seen that these curves are very much flatter than those of the  $\frac{1}{4}$  in. rod and the  $\frac{3}{16}$  in. rod which follows this one.

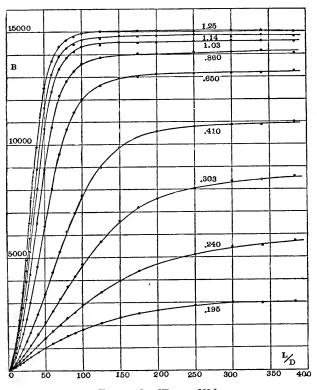


FIGURE 9. [TABLE IV.]

Curves showing variation of magnetic induction with different lengths of a Bessemer soft steel rod of diameter 0.4763 cm. The numbers affixed to the curves give the constant currents in amperes through the solenoid.

Figure 8 shows the original curves of October 9, 1906, and presented in Table IV.

From the data of these curves Figure 9 was also drawn. This shows the curves of constant current as the rod is increased in length. The numbers affixed to the curves give the current in amperes, so that the

applied field H' in the solenoid can be found by multiplying by the factor 20.5. It is seen that at first the induction increases very rapidly and nearly linearly. Then after a sharp bend the curve approaches a maximum induction asymptotically. It is interesting to see how for higher currents this maximum is reached very much sooner

TABLE III. [FIGURE 7.] October 4, 1906. Diam. = 1.270 cms. = 1.12 in.REVERSALS.

| В.    |        | Values of $N 	imes 10^4$ . |     |     |     |     |    |    |            |     |     |     |  |
|-------|--------|----------------------------|-----|-----|-----|-----|----|----|------------|-----|-----|-----|--|
| Б.    | m = 10 | 20                         | 30  | 40  | 50  | 60  | 70 | 80 | 90         | 100 | 120 | 144 |  |
| 1000  | 1820   | <b>5</b> 90                | 300 | 190 | 126 | 95  |    |    |            |     |     |     |  |
| 2000  |        | 614                        | 317 | 198 | 135 | 97  | 74 | 62 | 50         | 42  | 31  | 23  |  |
| 3000  |        | 635                        | 325 | 203 | 137 | 99  | 76 | 63 | 50         | 42  | 31  | 23  |  |
| 4000  |        |                            | 831 | 204 | 139 | 100 | 76 | 62 | 50         | 42  | 31  | 23  |  |
| 5000  |        |                            | 331 | 204 | 139 | 100 | 76 | 62 | 50         | 41  | 30  | 23  |  |
| 6000  |        |                            | 331 | 204 | 139 | 100 | 76 | 62 | <b>5</b> 0 | 40  | 30  | 23  |  |
| 7000  |        |                            |     | 205 | 139 | 100 | 76 | 61 | 49         | 40  | 28  | 21  |  |
| 8000  |        |                            |     | 205 | 139 | 100 | 76 | 61 | 49         | 39  | 28  | 20  |  |
| 9000  |        |                            |     | 203 | 139 | 100 | 75 | 60 | 48         | 39  | 27  | 19  |  |
| 10000 |        |                            |     |     | 137 | 99  | 78 | 59 | 48         | 38  | 27  | 19  |  |
| 11000 |        |                            |     |     | 132 | 99  | 70 | 57 | 46         | 36  | 26  | 19  |  |
| 12000 |        |                            |     |     | 123 | 90  | 66 | 54 | 42         | 33  | 24  | 18  |  |
| 13000 |        |                            |     |     |     |     | 59 | 47 | 38         | 29  | 21  | 16  |  |
| 14000 |        |                            |     |     |     |     |    |    |            |     |     |     |  |
| 15000 |        | • •                        |     |     |     |     |    |    | • •        |     |     |     |  |

than for lower currents. As regards curvatures, the sharp bend, and approach to a maximum value, these curves bear a close resemblance to the magnetization curves, when plotted on the I vs. II' plane.

See Figure 10 for the magnetization curves accompanying Table V. October 20, 1906. These are also quite steep.

No figure is given for the results obtained on November 6, 1906, and collected in Table VI. The curves are very steep.

See Figure 11 for the magnetization curves corresponding to Tables VII and VIII, of November 16, 1906. The curves passing through the crosses are the ones obtained by using the method of steps, while the

TABLE IV. [FIGURE 8.]

October 9, 1906.

Diam. = 0.4763 cm. = 3/16 in.

REVERSALS.

| В.    | Values of $N \times 10^4$ . |      |     |     |     |     |     |     |    |    |    |     |     |     |     |     |
|-------|-----------------------------|------|-----|-----|-----|-----|-----|-----|----|----|----|-----|-----|-----|-----|-----|
| D.    | m = 10                      | 15   | 20  | 25  | 30  | 40  | 50  | 60  | 70 | 80 | 90 | 100 | 125 | 150 | 175 | 200 |
| 1000  | 2001                        | 1023 | 638 | 434 | 319 | 196 | 133 |     |    |    |    |     |     |     |     |     |
| 2000  |                             | 1049 | 659 | 449 | 329 | 199 | 132 | 99  | 79 | 60 | 51 | 42  | 28  | ٠.  |     |     |
| 3000  |                             |      | 665 | 458 | 331 | 205 | 135 | 101 | 79 | 61 | 52 | 41  | 28  | 20  | 15  | 12  |
| 4000  |                             |      |     | 461 | 336 | 209 | 140 | 104 | 79 | 61 | 51 | 41  | 28  | 20  | 16  | 13  |
| 5000  |                             |      |     | 461 | 335 | 206 | 140 | 104 | 78 | 61 | 51 | 41  | 28  | 19  | 14  | 11  |
| 6000  |                             |      |     |     | 336 | 205 | 140 | 103 | 78 | 61 | 51 | 41  | 28  | 19  | 14  | 11  |
| 7000  |                             |      |     | ٠.  |     | 204 | 139 | 103 | 78 | 60 | 49 | 41  | 28  | 19  | 14  | 11  |
| 8000  |                             |      |     |     |     | 204 | 138 | 102 | 77 | 59 | 48 | 40  | 28  | 19  | 13  | 11  |
| 9000  |                             |      |     |     |     | 204 | 137 | 100 | 76 | 58 | 47 | 39  | 27  | 18  | 13  | 10  |
| 10000 |                             |      |     |     |     | 201 | 135 | 99  | 75 | 57 | 46 | 38  | 26  | 18  | 13  | 10  |
| 11000 |                             |      |     |     |     |     | 132 | 97  | 72 | 56 | 45 | 35  | 24  | 17  | 13  | 9   |
| 12000 | ٠.                          |      |     |     |     |     | 130 | 94  | 68 | 53 | 43 | 33  | 22  | 15  | 12  | 9   |
| 13000 |                             |      |     | ٠.  |     |     | 122 | 90  | 65 | 50 | 40 | 30  | 20  | 13  | 12  | 9   |
| 14000 |                             |      |     |     |     |     |     | 83  | 58 | 42 | 33 | 25  | 18  |     |     |     |
| 15000 |                             |      | ٠.  |     |     |     |     |     |    |    |    |     |     |     |     |     |

ones through the dots were found by means of the reversal method. The vertical arrow-points indicate the probable position of the normal curve by steps, and the oblique arrows give the reversal one. Several series of step curves were taken for each  $\mathfrak{m}$  so that a good average curve could be constructed. It will be noticed that the step curves all lie below the others, except the one for  $\mathfrak{m}=400$ .

No figure was made for the curves, which are exhibited statistically in Table IX, of December 1, 1906.

The work up to this point indicates that the thicker rods have smaller demagnetizing factors than the thin rods. To test this matter

TABLE V. [FIGURE 10.]

October 20, 1906.

Diam. = 0.3969 cm. = 5/32 in.

REVERSALS.

|       |        |     |     | Val | ues of | <i>N</i> · | 104. |     |     |     |     |     |     |
|-------|--------|-----|-----|-----|--------|------------|------|-----|-----|-----|-----|-----|-----|
| В.    | m = 30 | 40  | 50  | 60  | 70     | 80         | 90   | 100 | 125 | 150 | 200 | 250 | 300 |
| 1000  | 327    | 199 | 133 | 95  | 74     | 59         | 48   | 38  | 23  | 22  | 16  |     |     |
| 2000  | 345    | 211 | 141 | 103 | 80     | 62         | 49   | 41  | 30  | 20  | 11  | 7   | 5   |
| 3000  | 353    | 216 | 145 | 107 | 82     | 64         | 50   | 42  | 29  | 20  | 11  | 7   | 5   |
| 4000  | 354    | 216 | 148 | 107 | 82     | 64         | 51   | 42  | 29  | 20  | 12  | 8   | 6   |
| 5000  | 357    | 217 | 147 | 107 | 83     | 64         | 52   | 42  | 29  | 20  | 12  | 7   | 6   |
| 6000  | 355    | 216 | 146 | 107 | 82     | 64         | 52   | 42  | 29  | 20  | 12  | 7   | 5   |
| 7000  |        | 217 | 147 | 108 | 83     | 64         | 52   | 42  | 30  | 20  | 11  | 8   | 6   |
| 8000  |        | 217 | 145 | 107 | 82     | 64         | 52   | 42  | 28  | 20  | 11  | 7   | 5   |
| 9000  |        | 215 | 146 | 107 | 82     | 64         | 52   | 42  | 28  | 20  | 11  | 7   | 6   |
| 10000 |        | 214 | 145 | 106 | 81     | 63         | 51   | 42  | 27  | 20  | 12  | 8   | 6   |
| 11000 |        | 214 | 144 | 107 | 80     | 62         | 49   | 41  | 27  | 20  | 12  | 8   | 7   |
| 12000 | . ,    | 214 | 143 | 104 | 79     | 60         | 48   | 40  | 26  | 19  | 12  | 10  | 9   |
| 13000 |        |     | 141 | 102 | 76     | 59         | 46   | 38  | 24  | 18  | 18  |     |     |
| 14000 |        |     | 130 | 93  | 70     | 54         | 41   | 34  | 19  | 16  | 14  |     |     |
| 15000 |        |     |     | 79  | 60     | 48         | 82   | 27  | 17  | 14  |     |     |     |

more carefully, a very long solenoid was built, probably the only one of its size ever constructed. The wire was wound in a double coil over a thick brass tube, making in all eight layers. The wire used was the Annunciator No.18, of diameter = 1 mm., with red insulation. The dimensions of the solenoid are:

Length of windings = 485.3 cms. = 15 ft. 11  $\frac{3}{16}$  in.

Outside diameter = 5.96 cms. Inside diameter = 2.86 cms.

Number of turns = 10452 for each of the two coils.

## TABLE VI. [No Figure.]

November 6, 1906.

Diam. = 0.2381 cm. = 3/32 in.

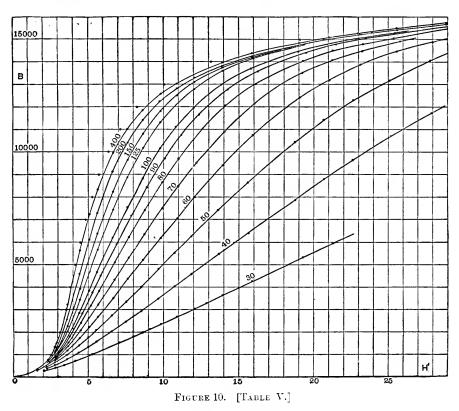
## REVERSALS.

| D     |        |     | Value | es of $N \times 1$ | 104. |     |     |
|-------|--------|-----|-------|--------------------|------|-----|-----|
| В.    | m = 50 | 60  | 80    | 100                | 150  | 200 | 300 |
| 1000  | (180)  | 102 | (54)  | 40                 | 19   |     |     |
| 2000  | (165)  | 110 | 63    | 42                 | 20   | (6) |     |
| 3000  | 160    | 110 | 65    | <b>4</b> 3         | 20   | (9) |     |
| 4000  | 160    | 113 | 67    | 43                 | 20   | 12  | (5) |
| 5000  | 159    | 113 | 67    | 43                 | 20   | 12  | 8   |
| 6000  | 159    | 114 | 68    | 43                 | 20   | 12  | 7   |
| 7000  | 158    | 113 | 67    | 43                 | 19   | 12  | 7   |
| 8000  | 158    | 113 | 66    | 42                 | 19   | 11  | 7 1 |
| 9000  | 157    | 112 | 65    | 42                 | 18   | 10  | 7   |
| 10000 | 159    | 112 | 64    | 41                 | 18   | 9   | 5   |
| 11000 | 158    | 112 | 63    | 39                 | 17   | 8   | (3) |
| 12000 | 153    | 108 | 61    | 36                 | 15   | 7   | (3) |
| 13000 | 150    | 104 | 58    | 34                 | 15   | 7   |     |
| 14000 | 143    | 97  | 50    | 29                 | 10   | 5   |     |
| 15000 |        |     | 38    | 22                 | 9    |     |     |

The two coils were used in parallel, so that the magnetizing field is H' = 27.064 e.g.s. units for each ampere.

The first rod tried in this solenoid was one of  $0.9525\,\mathrm{cm}$  diameter (=  $\frac{3}{8}$  inch), and was a complete failure, although it gave some very interesting results. No two consecutive step method magnetization curves would agree. The rod was 15 feet long, so that  $\mathfrak{m}=480$ .

The rod was carefully demagnetized and magnetized, apparently under similar conditions each time. Parts of eight different magnetization curves are shown in Figure 12 and illustrate the wide divergence at the higher inductions. The reason for this peculiar behavior of the fron was made clear when the rod was demagnetized and taken out of



Reversal magnetization curves for a Bessemer soft steel rod of diameter 0.3969 cm.

the solenoid, and then tested with a small pocket compass for consequent poles. It was found that the rod was quite strongly magnetized, and had polarity in the order N-N-N-N, the two middle poles being both near the middle of the rod. Evidently this rod had once been lifted around a warehouse by means of an electric crane with an electromagnet lifting device, so that it had been subjected to quite

a high magnetizing field. Besides, it is probable that the iron of this particular rod, which was not of the usual Bessemer steel, is not very homogeneous. In such cases it has been the experience of men who have had much to do with magnetization of iron in a practical way—as, for instance, Mr. Thompson, the mechanic of the Jefferson Physical

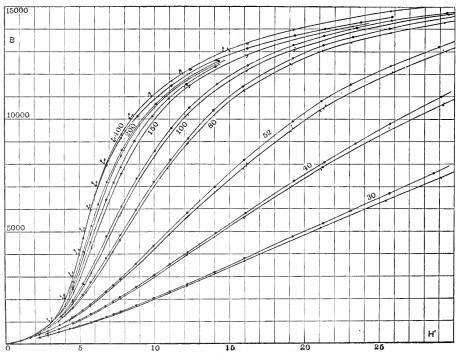


FIGURE 11. [TABLES VII AND VIII.]

Step and reversal magnetization curves for a Bessemer soft steel rod of diameter  $0.3175\ \mathrm{cm}.$ 

Laboratory — that heating the iron specimen white hot and then allowing it to cool slowly will not get rid of the consequent poles. Nor will subjecting the iron to higher magnetizing fields, and then decreasing the field while reversing constantly, so as to demagnetize, help the matter, for the poles come back straightway in their old positions.

After this the iron rods used in the long solenoid were carefully tested

for consequent poles before they were bought for the work. Even then some peculiarities were noted in the results, which are due to some irregularity in the polarity which was not apparent in the test with a small compass needle. It should be noticed that such irregularities as

TABLE VII. [FIGURE 11.]

November 16, 1906.

Diam. = 0.3175 cm. = 1/8 in.

Step Method.

| В.    |        |     | v   | alues of A | imes 104. |     |     |     |
|-------|--------|-----|-----|------------|-----------|-----|-----|-----|
| В.    | m = 30 | 40  | 52  | 80         | 100       | 150 | 200 | 400 |
| 1000  | 376    | 227 | 142 | 68         | 46        |     |     |     |
| 2000  | 382    | 230 | 145 | 69         | 46        | 22  | 11  |     |
| 3000  | 381    | 232 | 148 | 69         | 46        | 21  | 10  |     |
| 4000  | 382    | 230 | 149 | 69         | 46        | 22  | 11  | 1   |
| 5000  | 386    | 232 | 148 | 69         | 46        | 23  | 12  | 1   |
| 6000  | 388    | 232 | 149 | 69         | 46        | 23  | 12  | 1   |
| 7000  | 389    | 234 | 150 | 69         | 46        | 23  | 13  | 1   |
| 8000  |        | 234 | 150 | 69         | 46        | 23  | 13  | 1   |
| 9000  |        | 237 | 150 | 69         | 47        | 22  | 13  |     |
| 10000 |        | 237 | 149 | 68         | 45        | 22  | 12  |     |
| 11000 |        | 237 | 147 | 66         | 43        | 20  | 12  |     |
| 12000 |        |     | 146 | 65         | 42        | 20  | 12  |     |
| 13000 |        |     | 142 | 63         | 40        | 20  | 11  |     |
| 14000 |        |     |     |            |           |     |     |     |
| 15000 |        |     |     |            |           |     |     |     |

shown in Figure 12 are very much more pronounced when the step method is used. In fact, with the reversals it would probably turn out that a very smooth curve would be obtained, but which would lead to erroneous results in the demagnetizing factor.

No figure is given for the series whose results are tabulated in Table X, of January 16, 1907. This table should be compared with

that for the rod of same diameter worked out beginning on October 9. It will be noticed that these values for N are considerably larger than those of the earlier series. This again shows very clearly the difference between the reversal and the step method.

TABLE VIII. [FIGURE 11.] November 16, 1906. Diam. = 0.3175 cm. = 1/8 in. REVERSALS.

|       |         |     | V   | alues of I | V 	imes 104. |     |     |     |
|-------|---------|-----|-----|------------|--------------|-----|-----|-----|
| В.    | nt = 30 | 40  | 52  | 80         | 100          | 150 | 200 | 400 |
| 1000  | 365     | 224 | 136 | 64         | 44           |     |     |     |
| 2000  | 372     | 227 | 142 | 65         | 44           | 19  |     |     |
| 3000  | 371     | 227 | 143 | 65         | 44           | 19  | 10  |     |
| 4000  | 372     | 228 | 145 | 67         | 44           | 19  | 11  | 4   |
| 5000  | 372     | 228 | 142 | 67         | 45           | 20  | 12  | 4   |
| 6000  | 372     | 227 | 144 | 67         | 44           | 20  | 12  | 4   |
| 7000  | 372     | 228 | 144 | 67         | 44           | 20  | 12  | 4   |
| 8000  | 368     | 228 | 143 | 68         | 44           | 20  | 12  | 4   |
| 9000  |         | 228 | 142 | 66         | 43           | 19  | 11  | 4   |
| 10000 |         | 226 | 140 | 63         | 41           | 17  | 10  | 4   |
| 11000 |         | 222 | 134 | 59         | 38           | 15  | 9   | 4   |
| 12000 |         |     | 131 | 55         | 34           | 14  | 8   | 4   |
| 13000 |         |     | 125 | 49         | 30           |     |     |     |
| 14000 |         |     |     | 42         | (22)         |     |     |     |
| 15000 |         |     |     | ٠.         |              |     | ٠.  |     |

Figure 13 gives the experimental curves corresponding to Table XI, January 18, 1907. They were taken by the step method, and each curve was based on three or four separate magnetizations from zero to the highest value of H', so that good average results might be obtained. It will be noticed that the curve for  $\mathfrak{m}=200$  passes very nearly through two sets of observations, but that on either side of it lie

observation-points at quite a distance off. Most of the other curves are in much better agreement with their points. There were also taken a number of magnetization curves for the initial length of the rod, 15 feet, which made  $\mathfrak{m} = 329$ ; these curves resembled the ones

TABLE IX. [No FIGURE.] December 1, 1906. Diam. = 0.6350 cm. = 1/4 in. REVERSALS.

|       |         | Values of 1 | $	ext{V}	imes 10^4$ . |     |
|-------|---------|-------------|-----------------------|-----|
| В.    | m = 50. | 60          | 80                    | 100 |
| 1000  |         |             |                       |     |
| 2000  | 137     | 107         | 64                    | 39  |
| 3000  | 144     | 105         | 61                    | 39  |
| 4000  | 143     | 105         | 60                    | 38  |
| 5000  | 145     | 105         | 60                    | 40  |
| 6000  | 145     | 105         | 60                    | 38  |
| 7000  | 144     | 103         | 61                    | 39  |
| 8000  | 141     | 102         | 59                    | 38  |
| 9000  | 141     | 101         | 58                    | 37  |
| 10000 | 141     | 99          | 56                    | 37  |
| 11000 | 142     | 98          | 55                    | 36  |
| 12000 | 140     | 96          | 52                    | 34  |
| 13000 | 136     | 93          | 48                    | 33  |
| 14000 |         | 87          | 47                    | 32  |
| 15000 |         |             |                       |     |

for the rod with pronounced consequent poles. It thus appears that there must have been some irregularity in the demagnetized rod near one or perhaps both ends of the rod. As the rod was cut down from  $\mathfrak{m} = 329$  to  $\mathfrak{m} = 200$ , most of these irregularities were cut off. Then at the next shortening practically all the rest was eliminated. For m = 30a reversal curve, represented in the figure by crosses, was also taken.

See Figure 14 for the original curves, from  $\mathfrak{m}=15$  to  $\mathfrak{m}=240$ , from which Table XII, of January 22, 1907, was constructed. It will be seen that on the figure there appear a number of crosses. These represent magnetization curves, not actually drawn, which were taken with the

TABLE X. [No FIGURE.] January 15, 1907. Diam. = 0.4763 cm. = 3/16 in.

STEP METHOD. LONG COIL.

|       |        | Va  | alues of $N \times$ | 104. |     |
|-------|--------|-----|---------------------|------|-----|
| В.    | m = 80 | 100 | 150                 | 200  | 300 |
| 1000  | 66     | 40  | 18                  |      |     |
| 2000  | 66     | 43  | 19                  | 11   | 4   |
| 3000  | 65     | 43  | 20                  | 11   | 4   |
| 4000  | 66     | 43  | 20                  | 11   | 4   |
| 5000  | 66     | 43  | 21                  | 12   | 4   |
| 6000  | 66     | 42  | 22                  | 12   | 4.5 |
| 7000  | 66     | 42  | 21                  | 11   | 4.5 |
| 8000  | 65     | 42  | 20                  | 10.5 | 4   |
| 9000  | 65     | 42  | 19                  | 10.5 | 4   |
| 10000 | 64     | 41  | 18                  | 10.5 | 4   |
| 11000 | 62     | 40  | 18                  | 10.5 | 4   |
| 12000 | 59     | 38  | 16                  | 10   | 4   |
| 13000 | 54     | 33  | 15                  | 9    | 3   |
| 14000 | 47     | 28  | 14                  | 8    | 2   |
| 15000 | 37     | 25  |                     |      | 2   |

reversal method. This brings out a most interesting point. The thick brass tube opposes a sudden change in the magnetizing field, by virtue of eddy currents, and thus the establishment of the field is somewhat delayed and the magnetization of the iron takes place more slowly. The step method magnetization also is slower than the step method when used in a plain solenoid wound on a tube of pasteboard, as is the

first solenoid. But as the reversal method has now almost overtaken the step method, we may conclude that both are very nearly at their limiting positions, reached for very slow establishment of the magnetizing field, which are probably very nearly the same.

TABLE XI. [FIGURE 13.] January 18, 1907. Diam. = 1.111 cms. = 7/16 in.

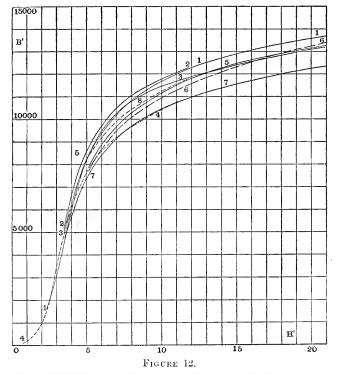
STEP METHOD. LONG COIL.

|       |         |     | V   | alues of $N$ | × 104. |     |     |     |
|-------|---------|-----|-----|--------------|--------|-----|-----|-----|
| В.    | nt = 30 | 40  | 50  | 60           | 80     | 100 | 150 | 200 |
| 1000  | 341     | 202 | 141 | 98           | 66     | 39  |     |     |
| 2000  | 347     | 208 | 144 | 103          | 66     | 41  | 20  | 11  |
| 3000  | 348     | 208 | 145 | 105          | 67     | 41  | 20  | 11  |
| 4000  | 348     | 207 | 146 | 106          | 66     | 41  | 21  | 11  |
| 5000  | 348     | 210 | 144 | 106          | 65     | 41  | 21  | 11  |
| 6000  | 351     | 211 | 145 | 106          | 66     | 41  | 22  | 11  |
| 7000  | 351     | 213 | 145 | 107          | 66     | 41  | 21  | 10  |
| 8000  | 351     | 214 | 145 | 107          | 66     | 41  | 21  | 10  |
| 9000  | 351     | 213 | 145 | 106          | 65     | 41  | 21  | 9   |
| 10000 |         | 210 | 144 | 104          | 63     | 40  | 20  | 8   |
| 11000 |         | 211 | 142 | 103          | 62     | 40  | 20  | 8   |
| 12000 |         |     | 140 | 100          | 60     | 38  | 20  | 7   |
| 13000 |         |     | 140 | 98           | 60     | 36  | 19  | 6   |
| 14000 |         |     |     | 93           | 59     | 35  | 19  | 4   |
| 15000 |         |     |     |              | 51     | 34  | 17  | 3   |

Figure 15 gives the original curves of Table XIII, taken on February 21, 1907, and following. As it was found that in the long solenoid the reversal method gives us practically the same results as the steps method, it was now used throughout because of its convenience and accuracy. Compared with the results of the rod of "cold rolled shafting" these values are somewhat smaller, but not more perhaps than is

due to the slight difference between the step and reversal methods which still remains. It is thus probable that the material of these two rods is not of very great importance. The curve for  $\mathfrak{m}=240$  was also taken, but was very nearly coincident with that for  $\mathfrak{m}=200$ .

When this rod, which we will call Rod No. I, was tested for consequent poles, there was also selected another one of the same diameter



Effect of consequent poles in an iron rod. The magnetization curves shown were taken under apparently the same conditions.

from the same lot of iron. Both were 20 feet long, and pieces of 1 foot and 4 feet were cut off from the ends. Rod No. II was magnetized at  $\mathfrak{m}=240$ , and gave the higher curve marked by the crosses. The pieces of 4 feet length had been mixed up so that it was impossible to say which belonged to Rod No. I and which to the other one. Test pieces of  $\mathfrak{m}=60$  were now prepared from both of these pieces, all of these rods of diameter 1.905 cms. being wound with 50 secondary turns

in the centre. The short rods now gave the magnetization curves which are merely indicated by crosses near the curves for  $\mathfrak{m}=80$  and  $\mathfrak{m}=60$  of Rod No. I. It is now evident which rod each of the small pieces came from. Of course the magnetic induction was now measured at a distance

TABLE XII. [FIGURE 14.]

January 22, 1907.

Diam. = 1.905 cms. = 3/4 in. Cold Rolled Shafting.

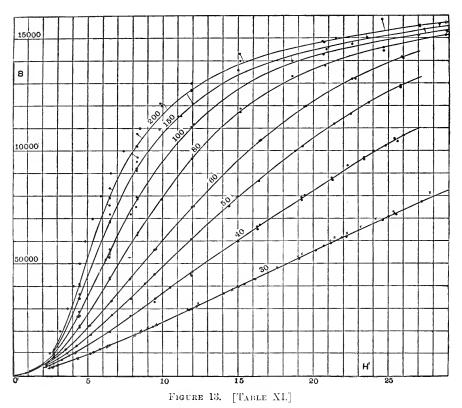
Step Method. Long Coll.

| В.    |        |      |     |     | Values | of $N \times$ | 104. |    |     |     |     |     |
|-------|--------|------|-----|-----|--------|---------------|------|----|-----|-----|-----|-----|
| Б.    | m = 10 | 15   | 20  | 30  | 40     | 50            | 60   | 80 | 100 | 150 | 200 | 240 |
| 1000  | 1960   | 1067 | 661 | 338 | 195    | 140           | 99   | 61 |     |     |     |     |
| 2000  | 1954   | 1064 | 663 | 333 | 198    | 147           | 100  | 63 | 40  | 23  |     |     |
| 3000  |        | 1075 | 673 | 342 | 203    | 150           | 107  | 63 | 41  | 21  | (6) |     |
| 4000  |        |      | 671 | 344 | 207    | 150           | 107  | 63 | 41  | 21  | 8   | 1   |
| 5000  |        |      | 669 | 344 | 208    | 148           | 106  | 63 | 41  | 21  | 9   | 2   |
| 6000  |        | ٠.   |     | 841 | 210    | 148           | 103  | 61 | 39  | 21  | 10  | 3   |
| 7000  |        |      |     | 342 | 210    | 146           | 102  | 60 | 38  | 21  | 12  | 5   |
| 8000  |        |      |     | 338 | 208    | 144           | 100  | 58 | 37  | 21  | 13  | 5   |
| 9000  |        |      |     | 341 | 207    | 141           | 98   | 58 | 36  | 19  | 13  | 5   |
| 10000 |        |      |     |     | 204    | 137           | 96   | 56 | 34  | 19  | 12  | 5   |
| 11000 |        |      |     |     | 200    | 134           | 93   | 54 | 32  | 19  | 12  | 5   |
| 12000 |        |      |     |     |        | 129           | 87   | 51 | 29  | 18  | 12  | 5   |
| 13000 |        |      |     |     |        | 124           | 81   | 47 | 25  | 18  | 12  |     |
| 14000 |        |      |     |     |        |               | 76   | 45 | 23  |     | 9   |     |
| 15000 |        |      |     |     |        |               |      |    |     | ٠.  |     |     |

of about 9.5 feet in the original 20 feet rods, but still the normal curves would probably not differ much. On the other hand, the normal curve for Rod No. I is quite different from that for Rod No. II.

With the help of the tracing cloth scale to be described below, Figure 16 was constructed, it being assumed that the maximum I is practivol. NLIII.—15

cally reached when B=17,000. This body of N-curves shows the curvatures which we were led to expect, and also the tremendous turn to the left as the curves get near the point of complete saturation. This curve might be said to embody the most important results obtained about the N-curves. The one corresponding to  $\mathfrak{m}=20$ , after going



Step magnetization curves in long coil for a Bessemer soft steel rod of diameter 1.111 cms.

out nearly straight far beyond the limits of the figure, sweeps back to the left and just shows in the upper left-hand corner. It will be noticed that the points of observation for all the curves become uncertain after  $B=12{,}000$ ; this is to be expected because the magnetization curves there become almost horizontal and run into one another, and the finding of the abscissa-differences is a very difficult matter.

## METHOD OF REDUCING OBSERVATIONS.

As a typical illustration of the whole work, let us consider the reduction of the observations taken on the largest iron rod used in the long

TABLE XIII. [FIGURE 15.]

February 21, 1907.

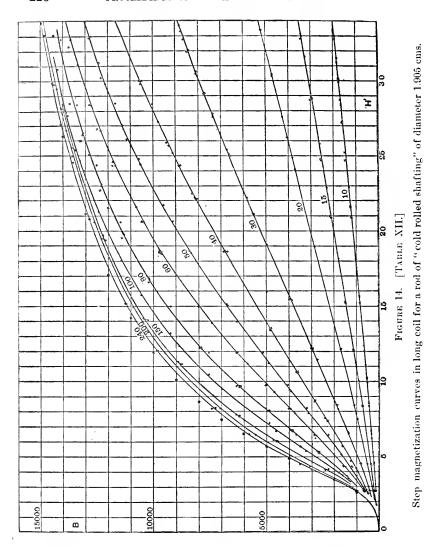
Diam. = 1.905 cms. = 3 4 in. Bessemer Steel.

REVERSALS IN LONG COIL.

| В.    | Values of $N 	imes 10^4$ . |     |     |     |     |     |             |     |     |     |
|-------|----------------------------|-----|-----|-----|-----|-----|-------------|-----|-----|-----|
|       | m = 15                     | 20  | 30  | 40  | 50  | 60  | 80          | 100 | 150 | 200 |
| 1000  | 1009                       | 658 | 332 | 201 | 139 | 98  | 64          | 39  | 20  | 9   |
| 2000  | 1019                       | 663 | 331 | 211 | 141 | 102 | 61          | 41  | 20  | 10  |
| 3000  | 1032                       | 668 | 386 | 209 | 140 | 102 | 62          | 41  | 21  | 10  |
| 4000  | 1032                       | 665 | 339 | 212 | 144 | 102 | 62          | 41  | 19  | 11  |
| 5000  | 1042                       | 657 | 340 | 213 | 142 | 103 | 63          | 42  | 20  | 11  |
| 6000  | 1045                       | 659 | 335 | 207 | 140 | 103 | 62          | 40  | 20  | 10  |
| 7000  | 1040                       | 662 | 335 | 207 | 141 | 102 | 61          | 40  | 20  | 11  |
| 8000  |                            | 662 | 335 | 204 | 138 | 99  | 58          | 38  | 21  | 12  |
| 9000  |                            | 661 | 332 | 200 | 136 | 97  | <b>อ</b> ้อ | 39  | 19  | 12  |
| 10000 |                            | 662 | 327 | 197 | 131 | 95  | 52          | 34  | 18  | 11  |
| 11000 |                            |     | 324 | 194 | 128 | 90  | 51          | 31  | 17  | 11  |
| 12000 |                            |     | 320 | 188 | 123 | 84  | 46          | 30  | 15  | 10  |
| 13000 |                            |     | 315 | 185 | 117 | 79  | 39          | 27  | 14  | 9   |
| 14000 |                            |     | 303 | 171 | 104 | 73  | 36          | 20  | 14  | 7   |
| 15000 |                            |     |     | 158 | 92  | 71  | 28          |     | 13  | 7   |

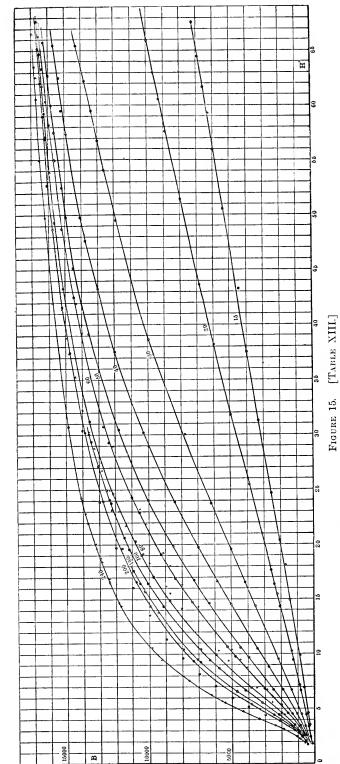
solenoid. This is the series on Rod No. I, begun on February 21. It usually takes about two days to take a series of observations, and the reductions and plotting of curves take about two or three days more.

When using the reversal method, the observations were taken under



the headings: current in solenoid, resistance in the box R', and ballistic throws observed. In the case of the step-by-step method the zero reading of the galvanometer was also necessary.

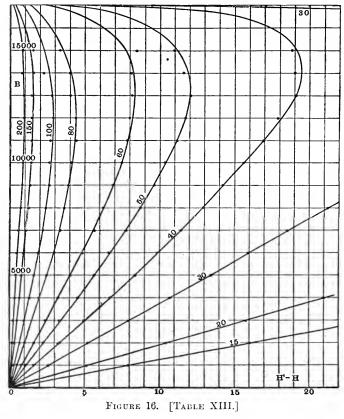
We start from the fundamental equation of a current through whose circuit the magnetic flux varies:



Reversal magnetization curves in long coil for rods of Bessemer soft steel of diameter 1.905 cms.

$$E - \frac{dN}{dt} = CR,$$

where E = electromotive force in the circuit, not due to changes in flux,



Back-shearing curves for Bessemer soft steel rod of diameter 1.905 cms.

N = total magnetic flux of induction through the circuit in the direction of the magnetic lines due to the current C, times the number of turns of wire in the circuit,

t = time variable,

C = actual current at time t flowing in the direction in which E acts,

R = total resistance of the circuit.

If we apply this equation to our secondary coil circuit, which includes the ballistic galvanometer, we have, since E = 0,

$$\Delta N = R \int_0^t C \cdot dt = RQ,$$

$$Q = \Delta N/R,$$

or

where Q = total charge through galvanometer,

 $\Delta N =$  number of flux-turns of change in the magnetic induction through the circuit.

This equation is expressed in e.g.s. units. If we use as our units the ampere, ohm, microcoulomb, and gauss, as we have done, then we must use the equation,

$$Q = \Delta N/(100R).$$
$$Q = T(S.$$

We have also

where T = actual throw in centimeters of scale reading produced by the discharge of Q microcoulombs through the galvanometer, and S = sensitiveness of galvanometer, expressed in centimeters of deflection obtained by discharging 1 microcoulomb through the galvanometer.

Now in the reversal method as used in these experiments,

$$\Delta N = 2 BA n = 2 B\pi (D/2)^2 n$$
,

where B = the magnetic induction in gausses, or number of lines of induction per square centimeter passing through the middle of the iron rod,

A =cross-section of rod in square centimeters,

n = number of turns of secondary coil wound around the middle of the rod,

D =diameter of the rod, as before.

This gives us

$$\frac{2 B\pi (D/2)^2 n}{100 \cdot R} = \frac{T}{S},$$

or

$$\frac{B}{T} = \frac{100 \cdot R}{2 |S\pi(D/2)|^2 \cdot n} \cdot$$

This formula is the most convenient for our purposes. As in our series we had the data

$$S = 1.489$$
  
 $D = 1.905$  cms.  
 $n = 50$  turns

$$\frac{B}{T} = \frac{100 \cdot R}{2(1.489) \pi (0.9525)^2 \cdot 50} \cdot$$

The right-hand member is a constant for any given R. In the work on the series of curves the R had values ranging from 117 to 7117 ohms; the galvanometer and secondary coil circuit having itself 117 ohms, of which the galvanometer had about 99 ohms, and the coil 18 ohms, the other resistance being added, when convenient, from the resistance box R'. The constants for these various R's were found and written down. Then all we have to do to find the B for any observation is to multiply the observed throw in centimeters by the proper constant. This was done either by means of logarithms or a very good slide rule.

If we use the step-by-step method, the formula simply drops the factor 2 and becomes,

$$\frac{\Delta B}{T} = \frac{100 R}{S\pi (D/2)^2 n} \cdot$$

For the long solenoid we have simply

$$H' = \frac{4 \pi N}{10 L} \text{ (No. of amperes used)}$$
$$= 27.064 \text{ (No. of amperes)}.$$

Having found the values of B and H, they were multiplied by 3 and 2 respectively, in order to facilitate the plotting of the points of observation. Then the magnetization curves were drawn by free-hand so as to fit the points as closely as possible.

This gives us the curves from m=15 to 200 in Figure 15. To find the corresponding normal curve  $(m=\infty)$  a graphical device was found to be of the very greatest utility. Not only was an enormous amount of time saved, which otherwise it would have been necessary to spend in almost endless computations, but the device was a positive aid in determining the position of the normal curve. On a large sheet of tracing cloth were drawn about seventeen horizontal lines, so that when properly placed over the sheet of millimeter paper on which the magnetization curves had been drawn, they coincided with the lines B=0, 1000, 2000, etc., up to 16,000. By means of lines radiating out from a point on the lowest of these horizontal lines, each one of the lines

above was divided into a large number of equal intercepts, each of which represented exactly 0.0010 of N, the demagnetizing factor, for the particular B corresponding to the line. The larger of these intercepts were further subdivided into tenths by means of short dashes, and each horizontal line was numbered for every 0.0010, beginning from zero on the left. Thus the tracing cloth was simply a large transparent scale through which the N corresponding to every H could be immediately read off. The error in the inaccurate spacing of the divisions of the scale was about 1 part in 200.

Now suppose we arbitrarily say for the moment that the N for the curve  $\mathfrak{m}=200$ , all along the curve, shall be 0.0016, or the value of N for the corresponding ellipsoid of revolution. By placing the tracing cloth so that any desired line coincides with its corresponding B below, and the magnetization curve for  $\mathfrak{m}=200$  crosses at N=16 units, we can read off the number of units for each of the other curves. After doing this for all of the horizontal lines of our scale, we have a table of values similar to that given for the rod of February 21, only the column for  $\mathfrak{m}=200$  will consist wholly of numbers 16.

This table is thus our first approximation. We may now put away our magnetization curve sheet with the scale, and proceed to get a better approximation by merely studying the table. It will be noticed that all the other columns will have values less than for the corresponding ellipsoids. The only logical thing to do is to decrease the 16's somewhat, at the same time decreasing every other number in the same row by the same amount, so as to give a table consistent as a whole when compared with the table for ellipsoids; and this gives us something similar to the table given. At the best approximation, the values for m = 200 will still be a unit or two in doubt, but this will make but a small error in the rods 30 to 50 diameters long. Of course individual values of N in the table are subject to errors in the drawing of the curve as well as observational errors, but when all the values of N for a certain length of rod are considered, a smooth curve could easily be drawn throughout the range of B in the experiment. We have, however, preferred to leave the tables as given directly from the last approximation.

Should any one not be quite satisfied with the values as tabulated for any one series of experiments, he may easily change the whole table to suit himself, but he must do this subject to the condition of adding or subtracting the same number for any one row as it is given here.

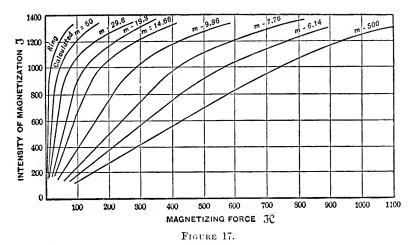
TABLE XIV.

| Observer.           | Method.            | D.            | L.                                                                                | Length<br>Sol-<br>enoid. | Н'.                                                  | Range in m used. | Remarks.                                                                 |                  |
|---------------------|--------------------|---------------|-----------------------------------------------------------------------------------|--------------------------|------------------------------------------------------|------------------|--------------------------------------------------------------------------|------------------|
| Ewing, 1885         | Ball.<br>Steps     | 0.158         | 47.5 to<br>7.9                                                                    |                          | 0-35                                                 | 300-50           |                                                                          |                  |
| Tanaka-             | Magn.              | (.100         | 9                                                                                 | 9.25                     |                                                      | 90               | Made in Japa:                                                            | n.               |
| daté, 1888          | Gauss A<br>Ewing's | (-153<br>-115 | 2-6<br>33.4                                                                       | 11.9<br>38.4             |                                                      | 13.1-39.2        | Made in Engla                                                            | ınd.             |
| C. R. Mann,<br>1895 | Magn.<br>Gauss A   | 2.370<br>237  | 11.850                                                                            | 30                       | 20-1300                                              | 5-50             | L constant,<br>turned down                                               | D                |
|                     | "                  | 1.924<br>1924 | 9.620                                                                             | 30                       | 22-660                                               | 5-50             | L constant,                                                              | D                |
|                     | **                 | 0.0836        | $25.08 \\ -4.18$                                                                  | 38.5                     | 2-300                                                | 300-50           | D constant, cut down.                                                    | L                |
| Benedicks,          | Magn.              | 0.8           | 20                                                                                | ·                        | 23-206                                               | 25               | All observation                                                          | ns               |
| 1902                | Ball.<br>Steps     | 0.8           | 20                                                                                |                          | 23-206                                               | 25               | made on hys<br>resis cycle<br>Normal cur<br>obtained by<br>lipsoid resul | es.<br>ve<br>el- |
| Jefferson           | Ball.              | 0.2381        | 182.8                                                                             | 207.7                    | 1 22 0                                               | 700 70           |                                                                          |                  |
| Physical            | _Rev.'s            | 0.2581        | -152.8 $-11.91$                                                                   | 207.7                    | 1-26.3                                               | 768-50           | 397 sec. turns.                                                          |                  |
| Laboratory,<br>1907 | 4.4                | 0.3175        | 182 8<br>9.53                                                                     |                          | 1-30                                                 | 576-30           | 230 " "                                                                  |                  |
|                     | Steps              | "             | **                                                                                | "                        | "                                                    | **               |                                                                          |                  |
|                     | Rev.'s             | 0.3969        | $182.8 \\ -11.91$                                                                 | "                        | 1–29                                                 | 461-30           | 180 " "                                                                  | ı                |
|                     | 66                 | 0.4763        | $182.8 \\ -4.76$                                                                  | 44                       | $\begin{array}{r} 3.4 \\ -22.3 \end{array}$          | 384-10           | 130 " "                                                                  |                  |
|                     | 66                 | 0.6350        | $182.8 \\ -6.35$                                                                  | "                        | -3.7 $-22$                                           | 288-10           | 100 " "                                                                  |                  |
|                     | "                  | "             | $\frac{-63.5}{-31.75}$                                                            | "                        | $\frac{4.7}{-30.8}$                                  | 100-50           | 30 " "                                                                   | İ                |
|                     | "                  | 1 270         | $     \begin{array}{r}       \hline       182.8 \\       -12.70     \end{array} $ | "                        | $\begin{array}{c c} \hline 3.4 \\ -20.3 \end{array}$ | 144-10           | 60                                                                       |                  |
|                     | Steps              | 0.4763        | $     \begin{array}{r}       \hline       182.8 \\       -38.10     \end{array} $ | 485.3                    | 1.8-                                                 | 384-80           | 195 " "                                                                  |                  |
|                     | 44                 | 1.111         | 366.4<br>-33.33                                                                   | "                        | 1-34                                                 | 329.5<br>-30     | 50 " "                                                                   |                  |
|                     | Stepsand<br>Rev.'s | 1.905         | ${457.2}$ $-19.05$                                                                | "                        | 2.4-33.7                                             | 240-10           | 50 " "                                                                   | İ                |
|                     | Rev.'s             | 1.905         | $\frac{-}{457.2}$<br>-28.58                                                       | 44                       | 1.8-44                                               | 240-15           | 50 " "                                                                   |                  |

DISCUSSION OF INVESTIGATIONS ON THE DEMAGNETIZING FACTORS.

It was considered worth while to collate briefly the leading experimental conditions which have been used in the determinations of N for iron cylinders. Table XIV on the preceding page has therefore been constructed from available data.

It will be noticed that Mann used some very thick iron bars in the first two of his experimental series. However, a given diameter remained constant only throughout a single magnetization curve, say for  $\mathfrak{m}=5$ ; after this the bar was turned down to a smaller diameter on the lathe, so that  $\mathfrak{m}$  was thereby increased. If now the ballistically

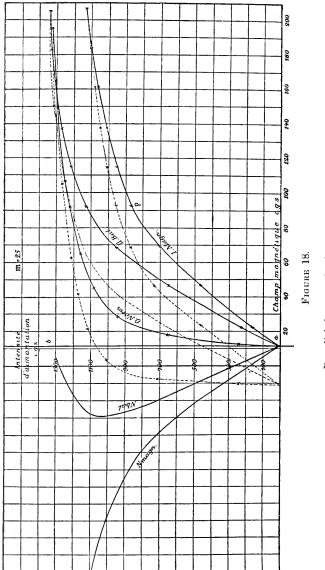


Mann's magnetization curves obtained magnetometrically. The bars vary in diameter from 2.370 cms, to 0.237 cm., while the length remains constant.

obtained results of the present paper can be at all related to magnetometric experiments on similar iron rods, they would lead us to expect that had Mann cut down his longest rod of 25.08 cms. from  $\mathfrak{m}=50$  to  $\mathfrak{m}=5$ , the values of N thereby obtained would not have agreed with those which he did get by turning down the bar from  $\mathfrak{m}=5$  to  $\mathfrak{m}=50$ . In fact the two sets of values for N, belonging to the two methods "sawing off" and "turning down" respectively, would probably have diverged more and more as  $\mathfrak{m}$  was decreased, the "turning down" values for N being always less because the diameters of the bars of this method are the greater, as carried out.

As noted in the outline at the head of this paper, Mann found that

the values of N as determined magnetometrically are nearly constant up to I=800, but after this they increase enormously. This behavior



Benedicks's magnetization curves.

of the N-curves is undoubtedly closely related to the change in the pole-distance ratio l/L, which probably approaches the value unity for complete saturation. The magnetization curves taken magnetometrically tend to diverge, or spread apart, for high magnetizations, whereas those taken ballistically all converge rapidly to the maximum ordinate  $I_{\infty}$ . Figure 17 is reproduced from Mann's paper, <sup>16</sup> and shows the curves from m=5 to m=50 obtained from his first cylinder. The method by which Mann gets at the position of the "normal" magnetization curve for an infinite rod is to assume that the magnetometric N for a cylindrical rod of m=300 is the same as for an ellipsoid of the same length and central cross-section, namely N=0.00075.

In his investigation Benedicks obtained the value of N for only one rod of hard steel (m = 25), but did this very thoroughly, using both the ballistic step and magnetometric methods. His normal curve is determined by transforming the steel cylinder into an ellipsoid of III = 30, obtaining magnetometrically the magnetization curve for this ellipsoid, and back-shearing this curve into the normal curve by means of the known demagnetizing factor for this ellipsoid, which is N = 0.0432. Theoretically the method is perfect, but we rather doubt whether it can be depended upon to give uniformly agreeing results in practice. The magnetization curves obtained by Benedicks are shown in Figure 18, which has been reproduced from his article 17. The figure shows the two types of N-curves, — the magnetometric and the ballistic. — and their opposite behavior for high magnetizations. Benedicks also publishes the N-curves as he derives them from Ewing's original six curves, all showing a behavior similar to that of his own curve  $N_{ad}$ . These N-curves are practically identical with those shown in Figure 19 of this paper; these were determined by our methods directly from Ewing's curves shown in Figure 2, which were reconstructed from the original figure 18 in order to have both figures on exactly the same scale as our own curves, for purposes of comparison. See Figure 16, which shows the N-curves for our Bessemer steel rod of diameter 1.905 cms.

We might note that Benedicks gets no curvature in the N-curve near the origin, because he takes his observations from hysteresis cycles of magnetization, the maximum applied field being about H' = 206 units.

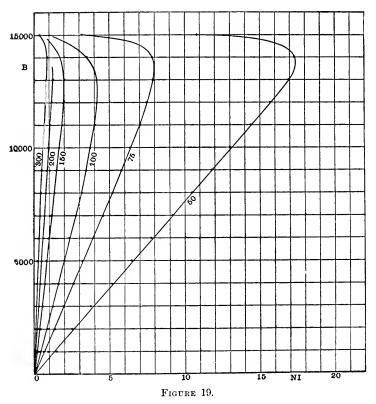
Benedicks criticizes Mann's assumption that N = 0.00075 for an

<sup>16</sup> Phys. Rev., 3, 359-369 (1896).

<sup>17</sup> Bihang Svenska, Vet.-Akad. Handlingar, 27 (1), No. 4, 14 pages (1902).

<sup>18</sup> Phil. Trans., 176 (1885), Plate 57, Figure 3.

iron cylinder of m = 300, as being unwarranted. He determines N by both the ballistic and magnetometric methods for a rod of m = 300 by back-shearing the ballistic curve into the normal curve, using  $N_{bal} = 0.0005$ , according to Du Bois, thus finding the N to be 0.0028 for the magnetometric method. He would, therefore, correct Mann's



Back-shearing curves for Ewing's soft iron wire of diameter 0.158 cm. Determined from results found in the present paper.

values of N by adding 0.0020 to each N throughout. Now it seems to us quite clear, as remarked somewhere in the earlier part of this paper, that we have no right to assume that the normal I vs. H curve, as obtained ballistically, should be even approximately the same as the Mean I vs. Mean H curve of the magnetometric method. This assumption is rendered particularly doubtful when we see the very wide

difference between the magnetization curves for m = 300 by the ballistic and magnetometric methods as observed by Benedicks and published in the "Bihang," and when we consider at the same time that both these curves cannot possibly be very far away from their

TABLE XV. VALUES OF N.

|     |            |          | Cylinder.  |                  |         |                |  |  |
|-----|------------|----------|------------|------------------|---------|----------------|--|--|
| m.  | ELLIPSOID. |          | Ballistic. |                  |         | Magnetometric. |  |  |
|     |            | Du Bois. | Benedicks. | Jeff. Phys. Lab. | Mann.   | Benedicks.     |  |  |
| 5   | 0.7015     |          |            |                  | 0.68000 |                |  |  |
| 10  | 0.2549     | 0.2160   |            | 0 1820-0.2001    | 0.25500 |                |  |  |
| 15  | 0.1350     | 0.1206   |            | 0.1000-0.1075    | 0.14000 |                |  |  |
| 20  | 0.0848     | 0.0775   |            | 0.0635-0.0671    | 0.08975 |                |  |  |
| 25  | 0.0579     | 0.0533   | 0.0444     | 0.0445-0.0465    | 0.06278 | 0.0658         |  |  |
| 30  | 0.0432     | 0.0393   |            | 0.0331-0.0388    | 0.04604 |                |  |  |
| 40  | 0.0266     | 0.0238   |            | 0.0204-0 0234    | 0.02744 |                |  |  |
| 50  | 0.0181     | 0.0162   |            | 0.0139-0 0160    | 0.01825 |                |  |  |
| 60  | 0.0132     | 0.0118   |            | 0.0100-0.0116    | 0.01311 |                |  |  |
| 70  | 0.0101     | 0.0089   |            | 0.0076-0.0088    | 0.00988 |                |  |  |
| 80  | 0.0080     | 0.0069   |            | 0.0060-0.0069    | 0.00776 |                |  |  |
| 90  | 0.0065     | 0.0055   |            | 0.0050~0.0056    | 0.00628 |                |  |  |
| 100 | 0.0054     | 0.0045   |            | 0.0041-0.0046    | 0.00518 |                |  |  |
| 125 | 0.0036     |          |            | 0.0028-0.0032    |         |                |  |  |
| 150 | 0.0026     | 0.0020   |            | 0.0019-0.0023    | 0.00251 |                |  |  |
| 200 | 0.0016     | 0.0011   |            | 0 0011-0.00125   | 0.00152 |                |  |  |
| 300 | 0.00075    | 0.0005   |            | 0.0004-0.0007    | 0.00075 |                |  |  |

limiting positions for the infinite rod. On the other hand it is quite reasonable to suppose that the N for any iron ellipsoid is always greater than the N for the corresponding cylinder, obtained by either of the two methods; because by adding the extra mass of iron to an

TABLE XVI. THE DEMAGNETIZING FACTORS IN THE RANGE OF PRACTICAL CONSTANCY.  $Reversals \ in \ Short \ Coil \ ;$ 

| 111.                                              | D = 0.2381.                       | 0.3175.                          | 0.3969.                                       | 0.4763.                                                | 0.6350.                                                  | 1.270.                                                     |
|---------------------------------------------------|-----------------------------------|----------------------------------|-----------------------------------------------|--------------------------------------------------------|----------------------------------------------------------|------------------------------------------------------------|
| 10<br>15<br>20<br>25<br>30<br>40<br>50            | 159<br>113                        | 372<br>228<br>(155)<br>(113)     | 355<br>216<br>147                             | 2001<br>1049<br>665<br>461<br>336<br>206<br>140<br>103 | 1990<br>1028<br>653<br>(458)<br>332<br>205<br>139<br>101 | 1820<br>(1000)<br>635<br>(445)<br>331<br>204<br>139<br>100 |
| 70<br>80<br>90<br>100<br>125<br>150<br>200<br>300 | 67<br>(54)<br>48<br>20<br>12<br>7 | 67<br>(54)<br>44<br><br>20<br>12 | (81)<br>64<br>52<br>42<br>29<br>20<br>12<br>6 | 78<br>61<br>51<br>41<br>28<br>19+<br>11+               | 76<br>60<br>(50)<br>41<br>28<br>19                       | 76<br>62<br>50<br>41<br>(28)<br>                           |

TABLE XVII.

Principle of Step Method:

| ın.                                                                                        | Du Bois. $D = 0.158$ .                                                               | D = 0.3175.                                                  | 0.4763. | 1,111.                                 | 1.905.                                                                       | 1.905<br>(Rev.'s<br>in Long<br>Coil).                                    | Percentage<br>Difference<br>between 0.3175<br>and 1.905. |
|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------|---------|----------------------------------------|------------------------------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------|
| 10<br>15<br>20<br>25<br>30<br>40<br>50<br>60<br>70<br>80<br>90<br>100<br>125<br>150<br>200 | 2160<br>1206<br>775<br>533<br>393<br>238<br>162<br>118<br>89<br>69<br>55<br>45<br>20 | 388<br>234<br>(160)<br>(116)<br>(88)<br>69<br>(56)<br>46<br> | 66      | 350<br>212<br>145<br>106<br><br>41<br> | 1960<br>1075<br>671<br>(465)<br>843<br>209<br>149<br>106<br><br>63<br><br>21 | 1045<br>662<br>(455)<br>336<br>209<br>142<br>103<br><br>62<br><br>41<br> | 15 5 % 12 " 11 " 11 " 10 " 12.2 " 15 " 14 "              |

The figures in parentheses are interpolated; all others have been obtained experimentally. For purposes of comparison, the values of Du Bois are given in Table XVII. The numbers given in these tables represent  $N \cdot 10^4$ , as in the earlier tables.

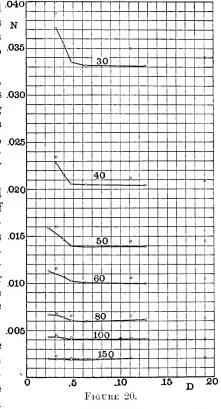
ellipsoid in order to form the corresponding cylinder, the surface magnetism  $\sigma$  is shifted nearer to the ends of the rod and should exert less demagnetizing force. To be sure, we now have some volume magnetism,  $\rho = -$  Divergence I, in the cylinder, which does not exist in the ellipsoid, but the effect of this

is probably always extremely small. On the whole we feel .040 certain that Mann's value is N quite near the truth, and is probably even a trifle too .035 large.

Table XV, on page 239, gives briefly all the results .030 obtained on demagnetizing factors for the region in which they are practically constant, .025 that is, for the iron cylinders up to about I = 800, or B = 10,000.

The values of N as obtained for the various diameters of rods in the present investigation are given in Tables of XVI and XVII on the preceding page. They were taken from the tables given for each separate rod, and are fairly constant over the range from B = 3000 to B = 9000.

The values of N of these tables have been plotted in Figure 20 against the corresponding diameters of the rods. The points connected by straight lines are the reversal method values, while those left unconnected are the ones taken by the principle of stars. It seems to



Curves showing the variation in N for different diameters of iron rods. The numbers near curves give the corresponding values of m.

ciple of steps. It seems to be shown that the values of N experience a rapid drop from D = 0.238 to about D = 0.50, and then remain nearly constant as the diameter is further increased.

For practical use in finding permeabilities Table XVIII has been vol. XLIII. — 16

constructed. The induction is assumed to be observed experimentally by the step method, and the K of the table is used in the equation

H = H' - KB.TABLE XVIII.

|     | VALUES OF K. |                        |  |  |  |
|-----|--------------|------------------------|--|--|--|
| 111 | D = 0.3175   | D = 1.1  to  2.0  cms. |  |  |  |
| 15  |              | 0.00852                |  |  |  |
| 20  |              | 0.00533                |  |  |  |
| 25  |              | 0.00366                |  |  |  |
| 30  | 0.00309      | 0.00273                |  |  |  |
| 40  | 0.00186      | 0.00166                |  |  |  |
| 50  | 0.00127      | 0.00116                |  |  |  |
| 60  | 0.000925     | 0.000845               |  |  |  |
| 80  | 0.00055      | 0.000505               |  |  |  |
| 100 | 0.000366     | 0.000326               |  |  |  |
| 150 | 0.000183     | 0.000167               |  |  |  |

#### PROBLEM.

Suppose the magnetic susceptibility in a soft iron rod similar to Bessemer steel is to be tested ballistically. Suppose the rod is neither very thick nor long, and the ballistic galvanometer (Thomson) is not very sensitive. In order to get the greatest possible throw we may wind a large number of turns of wire of secondary coil around the middle of the rod, being careful not to exceed the point of maximum sensitiveness. This is reached when an additional turn of wire adds proportionately more resistance to that already in the galvanometer circuit than it adds turns to the total number of turns. Of course as long as the secondary coil is wound on in a single layer, and the resistance of the galvanometer is not negligible, this condition can never be reached; but where the coil is built up in several layers the resistance finally predominates. Suppose we have:

Galvanometer resistance = 12 ohms.

Sensitiveness = 0.0695 mm. throw per microcoulomb.

Dimensions of Iron Rod: Diameter = 5 mms. Length = 20 cms., so that  $\mathfrak{m}=40$ .

Secondary Coil: 480 turns of fine wire. Length = 3 cms. Resistance = 19.42 ohms.

We therefore neglect the leakage of induction through the secondary coil. If we have no extra resistance in the galvanometer circuit the formula gives for the method of reversals:

$$\frac{B}{T} = \frac{100 \cdot R}{S \cdot 2 \, \pi (0.25)^2 480} = \frac{42 \cdot 31}{0.00695 \, \pi \cdot 0.60} = 2400.$$

This shows that we need no extra resistance for the secondary circuit.

Suppose we magnetize in a solenoid 31 cms. long and wound with 5 layers of wire, 113 turns in each layer. Then we have

$$H' = \frac{4 \pi 565}{10 \cdot 31} \cdot \text{(No. of amperes)} = 22.9 \text{ (amperes)}.$$

We get the following observations:

| Ballistic Throw.  |  |  |
|-------------------|--|--|
| 1.82 centimeters. |  |  |
| 2.59 "            |  |  |
| 3.36 "            |  |  |
| 3.97 "            |  |  |
| 4.55 "            |  |  |
| 5.02 "            |  |  |
|                   |  |  |

giving the calculated results:

| H'.   | В.    |
|-------|-------|
| 11.4  | 4370  |
| 15.2  | 6210  |
| 19.15 | 8070  |
| 22.3  | 9530  |
| 25.66 | 10900 |
| 28.80 | 12040 |
| 25.66 | 10900 |

Now taking N = 0.0217 for  $\mathfrak{m} = 40$ , we have

$$H = H' - NI = H' - KB$$

and  $K = N/4 \pi$ , since we may neglect H in comparison with B. We get, therefore,

$$K = 0.00173$$
,

and may now calculate H and the other quantities from the B of the above table. This gives us:

| $\Delta H = KE$ . | H.                                       | μ.                                                                | I.                                                                                         | κ.                                                                                                                                                                                     |
|-------------------|------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 7.55              | 3.85                                     | 1135                                                              | 348                                                                                        | 90                                                                                                                                                                                     |
| 10.73             | 4.47                                     | 1390                                                              | 493                                                                                        | 110                                                                                                                                                                                    |
| 13.94             | 5.21                                     | 1548                                                              | 641                                                                                        | 123                                                                                                                                                                                    |
| 16.47             | 5.83                                     | 1634                                                              | 758                                                                                        | 130                                                                                                                                                                                    |
| 18.85             | 6.81                                     | 1600                                                              | 865                                                                                        | 127                                                                                                                                                                                    |
| 20.82             | 7.97                                     | 1520                                                              | 960                                                                                        | 120                                                                                                                                                                                    |
|                   | 7.55<br>10.73<br>13.94<br>16.47<br>18.85 | 7.55 3.85<br>10.73 4.47<br>13.94 5.21<br>16.47 5.83<br>18.85 6.81 | 7.55 3.85 1135<br>10.73 4.47 1390<br>13.94 5.21 1548<br>16.47 5.83 1634<br>18.85 6.81 1600 | 7.55     3.85     1135     348       10.73     4.47     1390     493       13.94     5.21     1548     641       16.47     5.83     1634     758       18.85     6.81     1600     865 |

We chose the value of N as would correspond to the ballistic step method. Had we, however, used the method of reversals with a solenoid wound on a pasteboard tube, or a split brass tube, then the ballistic throws observed would have been a little more than twice as great as those we found. If we take them as exactly twice as great, and if we assume that the time-constant of the solenoid is the same as for the short solenoid used in the earlier half of this work, then we should have

$$N = 0.0206$$
  $K = 0.00164$ 

and the calculated values of the demagnetizing fields, the resultant fields, and the permeabilities would be:

| Δ H   | H    | μ    |
|-------|------|------|
| 7.17  | 4.23 | 1030 |
| 10 20 | 5.00 | 1240 |
| 13.22 | 5.93 | 1360 |
| 15.60 | 6.70 | 1420 |
| 17.90 | 7.76 | 1410 |
| 19.70 | 9.10 | 1320 |

This shows again how greatly different results obtained by step and reversal methods can be, if the observations are not properly corrected by using the appropriate N.

#### DISTRIBUTION OF MAGNETIC INDUCTION.

In our theoretical discussion of the shape of the N-curves we found, page 197, that we might expect that the magnetization is much nearer uniformity when the applied field H' is quite small, than it is in the region of large susceptibility. Now several articles have been published on the distribution of magnetic induction in iron rods, <sup>19</sup> but the magnetizing fields which these writers used were of much greater strength than are necessary in order to investigate this particular question. However, Benedicks <sup>20</sup> found a very neat inverse relation between the susceptibility  $\kappa$  and the pole-distance in a short bar magnet. This is very clearly shown by Figure 21, which has been reproduced from his article. The curve called "Distance des Poles" has the ordinates l/L, where L= actual length of the bar magnet, and l= distance between poles, the method of determining l being based on the formula

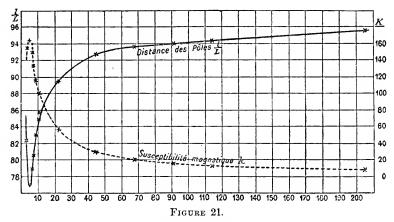
$$\frac{l}{L} = \frac{I_{\text{mean}}}{I_{\text{max.}}},$$

<sup>&</sup>lt;sup>19</sup> Phil. Mag., (5), **46**, 478-494 (1898), "On the Distribution of Magnetic Induction in Straight Iron Rods," J. W. L. Gill; Phil. Mag., (5), **48**, 262-271 (1889), "On the Distribution of Magnetic Induction in a Long Iron Bar," C. G. Lamb.

<sup>&</sup>lt;sup>20</sup> Journ, de Physique, (4), **1**, 302-307 (1902), "Études sur la Distance des Pôles des Aimants"; Bihang Svenska Vet.-Akad. Handlingar, **27**, (1) No. 5, 23 pp. (1902), "Untersuchungen über den Polabstand Magnetischer Zylinder."

in which the  $I_{\text{mean}}$  is the magnetization as determined magnetometrically, and the  $I_{\text{max}}$  is found from the B as determined ballistically at the centre of the rod in the usual way. For this rod  $\mathfrak{m}=300$ . The abscissae represent H', the magnetic field applied from without. Similar curves had also been previously published by Dr. L. Holborn, <sup>21</sup> only the susceptibilities were taken directly from the unsheared magnetization curve of a short cylinder.

Although these experiments of Holborn and Benedicks practically prove the increased uniformity of magnetization for low fields, it is perhaps a better plan to settle this point by a more direct method. It was therefore thought that it might be of interest to compare the



Benedicks's curves, showing variation of the pole-distance ratio and the susceptibility in an iron rod. The abscissae give the field H' in c. g. s. units.

actual magnetic induction which passes through various cross-sections of some of our iron rods, for practically the whole range of magnetization from zero to saturation. To do this one might use a secondary search-coil, fitting loosely around the iron rod, which can be suddenly displaced along the rod by any desired distance. This would require two observers; but it could not be used conveniently in this work since the rods in which the magnetic induction was tested were 1.905 cms. in diameter, and the inner diameter of the brass tube around which the solenoid coils were wound was not much larger. Another method would be to wind coils around different parts of the rod and get the actual induction passing through each coil. This would do

<sup>21</sup> Sitzber, Akad. d. Wiss., Berlin, 1, 159-162 (1898).

well enough for the lower intensities of H' but would be an exceedingly insensitive method to use when the field H' is very high, since then the induction is nearly constant along the bar except at the very ends, so that the experimental error might easily be even greater than the actual difference in the magnetic induction between the central part of the rod and any other part. The best method seems to be to read the reversal method ballistic throw from a coil wound directly over the middle of the rod, and then, connecting any other coil, wound around the rod nearer the end, in series with the central coil but in opposition to it, observe the ballistic throw due to the difference in the flux

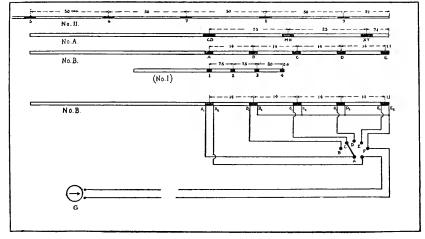


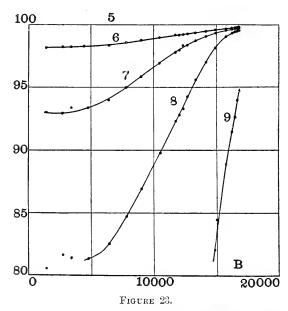
FIGURE 22.

Diagram showing arrangement of secondary coil and switch-board used in the work on the distribution of magnetic induction along an iron rod.

through the two coils. This was the idea adopted. Figure 22 shows diagrammatically the arrangement of the coils in one of the four different cases which were tried; the others were similarly arranged. The positions of all the secondary coils are shown in the diagrams drawn to scale and marked with the distances between the centres of the coils.

All the ends of the coils were led into small mercury cups in a small switchboard. The extremities  $B_2$ ,  $C_2$ ,  $D_2$ ,  $E_2$ , and one terminal of the ballistic galvanometer were all dipped into cup F. If now the copper connector is placed in the position A C as shown, then the ballistic throw observed on reversing the current in the primary solenoid is that

due to those lines of magnetic induction which thread through the centrally placed coil  $A_1 A_2$  and do not also pass through the coil  $C_1 C_2$ , provided we neglect the lengths  $A_1 A_2$  and  $C_1 C_2$  of the secondary coils in comparison with the distance  $A_1 C_1$  between the two coils. In other words, the ballistic throw measures the magnetic leakage between the coils which are connected in opposition. When the connector is placed across from A to F, then we get simply the throw



Curves showing variations in the distribution of magnetic induction in rod No. II.  $D=1.905~\mathrm{cms}$ , and m=240. The ordinate-axis represents percentage of magnetic induction.

due to the whole magnetic flux of induction through the central coil  $A_1 A_2$  in precisely the manner which was used in all of the preceding work on magnetization curves for different m's.

In this work on the distribution of the magnetic induction the extra resistance which had to be thrown into the galvanometer circuit by means of the resistance box R' in order to regulate the throw, varied greatly. For a connection like that shown in the figure usually no extra resistance was needed; in fact for low as well as for high magnetizing fields the magnetic induction approaches uniformity, so that in either case the ballistic throw is very low. Thus while in a certain

case m = 25, and B = 21120, the extra resistance R' had to be made as high as 10,000 ohms in order to keep the throw for the central coil alone from exceeding the length of the scale, yet when the coil nearest to the central one was connected in opposition to it, only a weak deflection was obtained with no extra resistance in the galvanometer circuit.

The curves which are shown represent four different rods, all having the largest diameter used, 1.905 cms., but two of these had the same length, the m being = 60, so that for these rods the results are combined in one figure. The data for these four rods are as follows:

Turns Maximum Bessemer Length Rodm. per Coil. of each Range of H'. Range of B. Battery D = 1.905. Coil. Voltage. No. II. 0.77 - 63.01620-16800 240 50 3.7 cms. 20 No. B. 60 50 2.3 0.50 - 66.884-16980 20 60 26 0.25-67.725-16800 20 No. A. 50 3.7 - 4400550-21120 (No. I) 25 110 1.3 40 No. of Bessemer Rod. Length of Solenoid. Distances between Coils in Cms. Coils.

TABLE XIX.

The coils are designated as follows, beginning with the central one:

5

5

4

485.3 cms.

107.2

No. II.

No. B.

No. A.

(No. I)

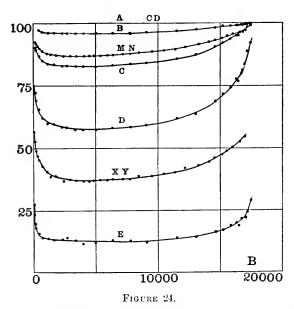
50, 50, 50, 50; 29 to end.

14, 14, 14; 1.1 to end.25, 25; 7.1 to end.

7.5, 7.4, 8.0; 0.4 to end.

The results are given graphically by Figures 23, 24, and 25 in this way: The induction B in the middle part of the rod, as found from reversing the current in the solenoid while only the central coil is included in the galvanometer circuit, is plotted horizontally; while the ordinates give the ratio of the corresponding inductions in the parts of

the rod surrounded by the other coils, to the induction at the centre. Thus, suppose for a given constant H' we had obtained throws corresponding to the central coil alone, and also for this coil when connected in opposition to every one of the other coils in turn. In an actual case we had for Rod  $B\colon H'=59.5$ , the induction for the central coil was B=16,560, leakage between CD and MN was 630, and between CD and MN was 630, and between MN considerable MN results we get for the actual magnetic induction through MN

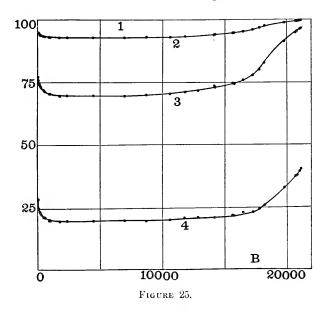


Curves showing variations in the distribution of magnetic induction in rods No. A and No. B. D=1.905 cms. and m=60.

15,920 lines, and through XY 8650 lines. Now, denoting the B through the central coil at any time by 100 per cent, we shall have 96.3 per cent of this induction passing also through the coil MN, and 52.3 per cent through XY. These two numbers are therefore plotted against B=16,560. Figures 23, 24, and 25 exhibit all the observations taken. The slight zigzag arrangement of the points is due to the fact that the current did not stay quite constant during the time of observing the throws from all the coils on a rod. All the rods have been referred to previously by the same designations, except (No. I), which is merely one of the end-pieces cut from the long rod

No. I mentioned before. The crossing of the curves for coils MN and C at a high induction is merely another instance of the great difference in magnetic quality of Rods A and B (or Rods I and II) which was already noticed in the magnetization curves of Figure 15.

From the curves in Figures 24 and 25 we see that for low fields there is quite an increase in the induction for coils not at the middle of the rod as compared with the induction through the central coil. This means that for these low fields the magnetization is more nearly



Curves showing variations in the distribution of magnetic induction in rod (No. I). D=1.905 cms. and  $\mathfrak{m}=25$ .

uniform. The range in H' for which the sharp upward bend of these curves occurs is precisely the same range for which the susceptibility changes most rapidly and is from H'=0 to about H'=5. After this we have quite a long interval for which the susceptibility is high, and the magnetization furthest removed from uniformity; here the curves showing percentage of induction as compared to that through the middle coils have their minimum and run along very nearly parallel to the B-axis. However, as the induction through the middle of the rod increases past B=10,000, all the curves begin to rise, slowly at first, then more rapidly. This indicates that the susceptibility is again

decreasing, and that the magnetization is becoming gradually more and more uniform. At about B = 17,000 the curves rise the fastest, showing that the middle portions of the rod are very nearly saturated and take up more magnetization only very slowly, while for the coils nearer the end the magnetization is still rapidly increasing. Figure 25, for the short rod ( $\mathfrak{m}=25$ ), shows that after B is about 20,000 under the middle coil, the curves all have points of inflection and now approach the ordinate 100 per cent asymptotically. If we now consider Figure 23, for the very long rod ( $\mathfrak{m} = 240$ ), we see that here we have a case of the magnetization being always very much nearer uniformity, so that the curves for coils 6, 7, and 8 are already in the asymptotic stage for B = 15,000 under the coil 5, and the points of inflection are near B = 10,000. When B = 15,000, the curve for the coil 9, nearest the end of the rod, shows a tremendous upward shoot from a long horizontal course near the ordinate 50 per cent. Since the figure only gives the observations in the range of percentages from 80 to 100, it might be well to give the missing values here:

| B in Coil 5. | Percentage : $rac{B_9}{B_5}$ . | B in Coil 5. | Percentage : $rac{B_9}{B_5}$ . |
|--------------|---------------------------------|--------------|---------------------------------|
| 2720         | 50.3                            | 11730        | 65.30                           |
| 3420         | 52.5                            | 12030        | 65.67                           |
| 4720         | 51.1                            | 12330        | 67.00                           |
| 6420         | 51.2                            | 12680        | 68.70                           |
| 7800         | 54.5                            | 13330        | 71.90                           |
| 9000         | 56.5                            | 14130        | 76.66                           |
| 10470        | 60.8                            |              |                                 |

In the case of the long rod the lowest fields used were still too high to show a rise in the curves, corresponding to increased uniformity of magnetization, as is seen in the other two figures.

The results show that near the middle of a rod the induction is practically the same for quite a little range, especially if the rod is fairly long. Thus the curve 6 in Figure 23 shows that in the rod of length about 458 cms. and  $\mathfrak{m}=240$ , the induction for a distance 50 cms. from the middle of the rod is always within about 2 per cent of the induction at the middle portion. And curve B in Figure 24 proves the induction at 14 cms. from the middle of the rod of length about

114 cms. and  $\mathfrak{m}=60$  to be always within about 4 per cent of the central induction. These facts justify the use of a secondary coil several cms. in length, provided the  $\mathfrak{m}$  of the rod is not too small.

The conclusion to be reached from the work on the induction distribution is that for low field-intensities, as well as for high ones, the magnetization of the iron rod is much more nearly uniform than it is in a long interval corresponding to rather high susceptibilities.

## DISCUSSION OF RESULTS OBTAINED.

When we look over the tables we readily see a number of interesting things. It is apparent that in general different methods or even different experimental conditions will give different normal curves, and hence different susceptibility curves. A striking result, and one which was obtained entirely unexpectedly, is that in the long solenoid, which was wound on a thick brass tube, the method of reversals agrees very closely indeed with the step-by-step method. This may in fact turn out to be quite a useful observation, for it points to the probability of getting values for the susceptibility of some kind of iron in the form of a short rod, which conform very closely to the ideal definition of susceptibility, which requires slow, continuous increase of the magnetizing field. Thus by winding our solenoid on very thick brass tubes, a large E. M. F. from a storage battery may be suddenly turned on, without giving almost instantaneously the full value of the magnetizing field within, on account of the eddy currents in the brass tube acting as a sort of "brake."

The most important results described in this paper about the demagnetizing factor N for cylindrical iron rods are the following:

- (1) The demagnetizing factor is not a constant, but shows two opposite curvatures, when plotted as abscissa-differences  $(H_i = NI)$  on the I vs.  $H_i$  plane; while for the highest values of I it falls to about  $\frac{1}{7}$  or  $\frac{1}{6}$  of its value for unsaturated I's.
  - (2) For values of B less than 10,000 the N is practically constant.
- (3) Using a solenoid made of wire wound on a non-metallic tube, or a split brass tube, the reversal method gives values for N considerably lower than the step-by-step method.
- (4) If the magnetizing solenoid is wound on a thick brass tube, the reversal and step methods practically agree, and values of N derived from curves taken in this way are regarded as the most desirable for scientific purposes, as they will give most accurate values for the susceptibility or the permeability of the iron.
  - (5) The demagnetizing factors are largest for thin rods. The differ-

ences between the corresponding N's for a rod of 0.3175 cm. diameter and one of 1.905 cms. diameter range from 10 to 16 per cent, both sets of values being taken to conform to the conditions stated in (4).

(6) Most of the rods used in this work have their N's in the range of practical constancy considerably smaller than the values given by Du Bois, but as the diameters of the rods decrease, a very close approach to Du Bois's values is obtained.

(7) The magnetization is furthest away from uniformity in the region of highest susceptibilities, and becomes more uniform for very

low as well as for very high applied fields.

In conclusion it is my pleasant duty and privilege to thank Professor B. O. Peirce for suggesting this research and for his constant interest in the work throughout the year. I also desire to state that the astaticised galvanometer system is due to the skill of Mr. John Coulson, Professor Peirce's assistant; and that the construction of the magnetizing solenoid was most successfully carried out by Mr. Thompson, the mechanic of the Jefferson Physical Laboratory.

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CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.—No. 17.

OUTLINES OF A NEW SYSTEM OF THERMODYNAMIC CHEMISTRY.

BY GILBERT NEWTON LEWIS.



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# OUTLINES OF A NEW SYSTEM OF THERMODYNAMIC CHEMISTRY.

BY GILBERT NEWTON LEWIS.

Received July 10, 1907.

In the rapid development of theoretical chemistry, in which the two laws of energy have played so important a rôle, two thermodynamic methods have been widely used. The first, employed by Gibbs, Duhem, Planck, and others, is based on the fundamental equations of entropy and the thermodynamic potential. The second, employed by such men as van't Hoff, Ostwald, Nernst, and Arrhenius, consists in the direct application to special problems of the so-called cyclic process.

The first method is general and exact, and has been a favorite with mathematicians and physicists, those who were already familiar with the use of the potential theory in mechanics. But unfortunately, except in name there is little analogy between physico-chemical equilibrium and the equilibrium in a mechanical system, and it is perhaps for this reason that the method has failed to commend itself to the majority of chemists. It must be admitted that it is the second method to which we owe nearly all of the advances that have been made during the last thirty years through the application of thermodynamics to chemical problems, and which is now chiefly used by investigators and in the text-books of physical chemistry.

Yet the application of this method has been unsystematic and often inexact, and has produced a large number of disconnected equations, largely of an approximate character. An inspection of any treatise on physical chemistry shows that the majority of the laws and equations obtained by the application of thermodynamics, are qualified by the assumption that some vapor behaves like a perfect gas, or some solu-

tion like a perfect solution.<sup>1</sup> As examples may be cited the mass law, the law of change of solubility with the temperature, the law of the lowering of vapor pressure by a solute, the law of Nernst for the electromotive force of a concentration cell, and many other equally important generalizations.

It is probable that no one of these laws is ever strictly true. As approximations to the truth they have been of the greatest service. But now that their utility has been demonstrated, the attention of a progressive science cannot rest upon their acknowledged triumphs, but must turn to the investigation of their inaccuracies and their limitations. From the study of the deviations from the simple gas laws has grown one of the most interesting chapters of chemistry. So from a study of the deviations from such a law as the mass law we may expect results of the highest value.

In such more exact investigations the old approximate equations of thermodynamic chemistry will no longer suffice. We must either turn to the precise, but rather abstruse, equations of entropy and the thermodynamic potential, or modify the methods which are in more common use, in such a way as to render them exact.

The latter plan is the one followed in the present paper, the aim of which is to develop by familiar methods a systematic set of thermodynamic equations entirely similar in form to those which are now in use, but rigorously exact.

The following development is necessarily brief and concise, but I have hoped, nevertheless, to make it intelligible to any chemist who is familiar with the simpler theorems of elementary calculus.

## THE ESCAPING TENDENCY.

The meaning of the term "escaping tendency" may be illustrated by an analogy taken from another branch of applied thermodynamics, — the theory of heat.

The conception of temperature owes its utility to the existence of two fundamental laws of heat exchange. When two bodies are brought together and there is no transfer of heat from one to the other, they are said to be at the same temperature; but if such a transfer takes place, the body which loses heat is said to be at a higher temperature than the other. Now the two laws of temperature are the following:

(1) Two bodies which have the same temperature as a third, have the

<sup>&</sup>lt;sup>1</sup> We may speak of a perfect solution as we speak of a perfect gas, that is, one which obeys the laws of an infinitely dilute solution.

same temperature as each other. (2) If a body A has a higher temperature than the body B, it has a higher temperature than any other body of the same temperature as B.

These are not self-evident truths, but empirical laws. If they did not exist, the idea of temperature would lose all value. Temperature determines the distribution of energy in a system, and we may regard the temperature of a body as a measure of the tendency of its internal heat to escape into other bodies.

There are in chemistry two laws which are in every way analogous to the laws of thermal exchange. If a system is composed of several parts, A, B, C, D, containing a given molecular species, X, the two fundamental laws concerning the distribution of X throughout the system are the following: (1) If when the phases A and B are brought together there is no transfer of X from one to the other, and if the same is true of A and C, then when B and C are brought together there will likewise be no transfer of X. (2) If X passes from the phase D to the phase A when they are brought together, then it will also pass from D to B, or to C, or to any phase which is in equilibrium with A as regards the distribution of X. It is obvious that these two laws follow directly from the fundamental laws of thermodynamies, for if they were not true a system could be constructed capable of perpetual motion.

The escaping tendency of a given molecular species in a given state is therefore analogous to temperature, and the two laws of escaping tendency are as follows: If the escaping tendency of a given molecular species, X, is the same in two phases, then X will not of itself pass from one phase to the other. If the escaping tendency of X is greater in one phase, it will pass from this phase into the other, when the two are brought together.

Let us illustrate the meaning of the escaping tendency by an example. When in a pure liquid a small quantity of some other substance is dissolved, the vapor pressure of the liquid is diminished, its freezing point is lowered, its boiling point is raised, its solubility in another solvent is diminished.<sup>2</sup> All these laws are comprised in the simple statement, that the escaping tendency of the solvent is diminished by the addition of the solute.

The idea of temperature was understood long before any suitable measure of temperature was found. Then the mercury thermometer was invented, later the gas thermometer, and finally in the absolute

<sup>&</sup>lt;sup>2</sup> So also the tendency of the liquid to take part in any chemical reaction is diminished, but until a later section of this paper our discussion will be limited to processes in which a given molecular species passes from one phase to another without any other change.

thermodynamic scale we possess the ideal measure of temperature. So indeed the idea of escaping tendency, although not distinctly formulated, has been tacitly recognized and used, and as a measure of the escaping tendency the vapor pressure has been employed. Now if all vapors obeyed the laws of a perfect gas, probably no better measure could be found. But this is never strictly the case, and the more the vapor departs from the ideal condition the more unsatisfactory is the vapor pressure as a measure of escaping tendency. By introducing a more satisfactory measure of escaping tendency we may gain advantages similar to those which resulted from the substitution of the absolute scale of temperature for the mercury scale.

Such a measure of the escaping tendency I have described and used in a previous paper.<sup>3</sup> It was called the fugacity, and so defined that the fugacity of a perfect gas is equal to its pressure. The fugacity of an imperfect gas differs, however, from the gas pressure by an amount which is greater, the more the gas deviates from the gas law.

The idea of fugacity is thus evolved from the use of vapor pressure as a measure of escaping tendency. When a substance is in equilibrium with its vapor, the fugacity, in order to fulfil the laws of escaping tendency, must be the same in both. The fugacity of a substance is therefore equal to its vapor pressure if the vapor behaves like a perfect gas. Speaking in terms not very precise, we may say that the fugacity of a substance is equal to the vapor pressure that the substance would have if its vapor were a perfect gas. It has been shown in the preceding paper that for a given substance in a given state the fugacity is a definite property of which the numerical value can in most cases be readily determined, and which is well suited to serve as an exact measure of the escaping tendency.

In many thermodynamic equations it is convenient to use concentrations instead of pressures. Likewise we shall find it desirable to introduce besides the fugacity, which has the dimensions of pressure, another quantity which has the dimensions of concentration. This quantity we will call the *activity*, and denote by the symbol  $\xi$ . The activity will be defined in terms of the fugacity,  $\psi$ , by the following equation,

$$\xi = \frac{\psi}{RT},$$

where R is the gas constant and T is the absolute temperature. Since the fugacity of a perfect gas is equal to its pressure, it is obvious that

<sup>&</sup>lt;sup>3</sup> The Law of Physico-Chemical Change. Zeit, phys. Chem., **38**, 205 (1901); These Proceedings, **37**, 49 (1901).

the activity of a perfect gas is equal to its concentration. If R has its ordinary value,  $\xi$  will be given in mols per liter.

Both the fugacity and the activity are well adapted to serve as measures of the escaping tendency. Indeed, for isothermal changes the equations in which the two quantities enter are as a rule identical. However, since the equations for the change of fugacity with the temperature are a little less simple than those of the activity, we shall choose the latter quantity for our present purpose. We shall start with a simple definition of the activity, and proceed to show that the change of the activity with the variables which determine the state of the system may be expressed by a series of exact equations which are of the same form as many of the familiar approximate equations for vapor pressure, solubility, etc.

On account of the large scope of this undertaking our consideration will be limited to those systems which are completely determined by the temperature, the pressure, and the composition of the various phases. How the work may be extended to include other variables, such as surface tension, has been indicated in the preceding paper.

## FUNDAMENTAL LAWS AND ASSUMPTIONS.

The following work will be based on the two laws of thermodynamics and upon the law that every gas and every solution as the concentration diminishes approaches as a limit the perfect gas and the perfect solution. Besides these we shall use the following definitions of the activity.

When the activity of a substance is the same in two phases, that substance will not of itself pass from one phase to the other.

When the activity of a substance is greater in one phase than in another, the substance will pass from the one phase to the other, when they are brought together.

The activity of a perfect gas is equal to its concentration.

The activity of the solute in a perfect solution, at constant temperature and pressure, is proportional to its concentration.

We shall see that these statements suffice to define the activity of a substance in any state, and except in unusual cases enable us to calculate its numerical value.

No further assumptions are necessary, but since our aim will be to lay stress rather on the exactness of the results obtained than upon the mathematical rigor of the method by which they are demonstrated, we shall adopt as working aids the following assumptions:

(1) For every molecular species we will assume that an ideal solvent

may be found (or imagined) in which that species dissolves to form a perfect solution, at all concentrations up to that of the saturated solution.

- (2) We may further assume that the ideal solvent chosen is one which suffers neither increase nor decrease of volume when the substance in question is dissolved at constant temperature and pressure. In other words, the volume of the ideal solution is the same as that of the ideal solvent it contains.<sup>4</sup>
- (3) In dealing with mixtures, use will be made of any kind of semipermeable membrane, real or imaginable, that may prove serviceable.

Probably in no case can the ideal solvent or the perfect semipermeable membrane be actually found. They will be employed as convenient fictions for the purpose of obtaining results which could be obtained without their aid, but by less simple methods.

# EQUATIONS OF A SOLUTION IN THE IDEAL SOLVENT.

Let us consider the vapor of a substance X, together with a solution of X in an ideal solvent. From the laws stated in the preceding section it may readily be shown that as the quantity of X is diminished, and the solution and the vapor become less concentrated, the ratio between the concentrations of X in the two phases approaches a constant value. In other words, if c represents the concentration of X in the solution, c' in the vapor, then at infinite dilution,

$$c' = \rho c$$
,

where  $\rho$  is a constant, when the temperature and pressure are constant, and may be called the distribution coefficient between solution and vapor at infinite dilution. This equation is merely the exact statement of Henry's law.

Since the two phases are kept in equilibrium, the activity of X must always be the same in one phase as in the other, that is,

$$\xi = \xi'$$
.

<sup>4</sup> This assumption is of minor consequence, and is introduced merely to simplify some of the mathematical work. It can be omitted without materially changing the following work.

<sup>&</sup>lt;sup>5</sup> Since our purpose is to develop a set of exact equations, but not to place too much emphasis upon the formal rigor with which those equations are obtained, it will not be necessary to repeat the proof of propositions which have already been proved elsewhere and which can obviously be obtained by familiar methods.

At infinite dilution the vapor of X becomes a perfect gas, and by definition

$$\xi^{l} = c^{l}$$
.

Hence at infinite dilution

$$\xi = e' = \rho e$$
.

 $\xi$  is the activity of X in the ideal solvent, and c is its concentration, and by definition  $\xi$  is proportional to c for all concentrations which we shall consider. Hence, not merely at infinite dilution but in general one of the fundamental equations of the ideal solution is,

$$\xi = \rho c.$$
 II\*6

From this another useful equation may be obtained. In the case of the ideal solution we have for the osmotic pressure,  $\Pi$ , the equation,

$$\Pi = cRT$$
.

Hence

$$\xi = \frac{\rho \Pi}{RT}.$$
 III\*

The quantity  $\rho$  varies with the temperature. In order to find the law of this variation we may once more consider the equilibrium at infinite dilution between the vapor of X and the solution of X in the ideal solvent.

Since we are dealing here with the ideal solution and with a perfect gas, the following special form of the equation of van't Hoff can be proved by familiar methods to be entirely exact.

$$\frac{d\ln\rho}{dT} = \frac{U_{(\text{IV})}}{RT^2},$$
 IV

where In signifies natural logarithm, and  $U_{(IV)}^{7}$  is the increase of internal energy when one mol of X passes from the ideal solvent into the infinitely attenuated vapor.

With the aid of these equations we are now prepared to undertake a systematic study of the laws of physico-chemical change. It is to be noted that from each one of the following exact equations two important approximate equations may be obtained directly,—one for solubility,

<sup>&</sup>lt;sup>5</sup> Numbered equations, such as those of the ideal solution, which are only true under special conditions, will be marked with the asterisk.

<sup>&</sup>lt;sup>7</sup> Since it will be necessary to use the symbol U for various kinds of internal energy change, a particular value of U will be designated by the number of the equation in which it first appears.

by substituting for the activity the concentration of a saturated solution, and one for vapor pressure, by substituting for the activity the concentration of the saturated vapor.

THE INFLUENCE OF PRESSURE AND TEMPERATURE UPON THE ACTIVITY OF A SIMPLE SUBSTANCE.

Let us consider a pure substance in any state, — solid, liquid, or gaseous, — and find the effect upon its activity: first, of a change of pressure at constant temperature, and second, of a change of temperature at constant pressure. Since the equations we are about to obtain are special cases of equations IX and XII, of which a complete proof is given in a later section, a less thorough derivation will here suffice.

In the preceding paper a formula was obtained (equation 14) for the influence of pressure on the fugacity of a pure substance, namely,

$$\left(\frac{\partial \ln \psi}{\partial P}\right)_T = \frac{v}{RT'},$$

where  $\psi$  is the fugacity and v the molecular volume. Combining this equation with equation I of the present paper, we find, since RT is constant,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_T = \frac{v}{RT}.$$

This is a perfectly general equation for the influence of pressure upon the activity of a pure substance. Since the second member of this equation is always a positive quantity, it is obvious that an increase of pressure always causes an increase in the activity.

In order to determine the influence of temperature, let us consider a substance X, in contact with its saturated solution in an ideal solvent. The solubility as measured by the osmotic pressure, II, varies with the temperature according to the well-known equation

$$\left(\frac{\partial \ln \Pi}{\partial T}\right)_{P} = \frac{Q}{RT^{2}}, \qquad VI^{*}$$

which, since we are dealing with the ideal solution, can be shown to be entirely exact. Q is the total heat absorbed when one mol of X dissolves reversibly in the ideal solvent. It is obviously the sum of three terms, — the increase in internal energy, the osmotic work done, and the work done against the external pressure, P. (According to one of our fundamental assumptions the volume of the ideal solvent does not

change when X dissolves.) The first of these terms we will call  $U_{\text{(VII)}}$ ; the second, according to the principle of van't Hoff, is equal to RT; and the third is equal to -Pv, where v is the molecular volume of pure X. We may write equation VI, therefore, in the form

$$\left(\frac{\partial \ln \Pi}{\partial T}\right)_{P} = \frac{U_{\text{(VII)}} + RT - Pv}{RT^{2}}.$$
 VII\*

Now the activity,  $\xi$ , of X in the pure state is always equal to that in the saturated solution. The latter is related to II, according to equation III, by the formula,

$$\Pi = \frac{\xi RT}{\rho}$$
.

Substituting this value of II in equation VII gives,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P} - \left(\frac{\partial \ln \rho}{\partial T}\right)_{P} + \frac{1}{T} = \frac{U_{(\text{VII})} + RT - Pv}{RT^{2}} \cdot$$

Substituting for the second term the value given by equation IV, and simplifying, we have,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P} = \frac{U_{(\text{VII})} + U_{(\text{IV})} - Pv}{RT^{2}} \cdot$$

 $U_{({
m VII})}$  is the increase in internal energy when a mol of X dissolves in the ideal solvent and  $U_{({
m IV})}$  is the increase when it passes from that solution into the state of infinitely attenuated vapor. The sum of these two is the increase in internal energy when a mol of X is evaporated and the vapor expanded indefinitely, or in other words it is the increase in internal energy when a mol of X evaporates into a vacuum. This important quantity, which we may call for the sake of brevity the ideal heat of evaporation, will be designated by the symbol Y. Substituting it in the last equation gives,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P} = \frac{\Upsilon - Pv}{RT^{2}}.$$
 VIII

This is the general equation for the effect of temperature on the activity of any pure solid, liquid, or gas. Except in very rare cases the second member is positive and  $\xi$  increases with T.

APPLICATIONS OF THE PRECEDING EQUATIONS.

A few examples will serve to illustrate the mode of application of equations V and VIII.

Two phases of the same substance, ice and water, for example, are in equilibrium at a given temperature and pressure. If the pressure on either phase alone is increased, the activity in that phase is increased, and the phase must disappear. If the pressure upon both phases is increased by the same amount, the activity is increased more in the phase of largest molecular volume, namely the ice, and it will disappear. By increasing the pressure on the ice by the amount dP, and that on the water by a greater amount, dP', it is possible to maintain equilibrium. Let us see what relation these two increments of pressure must bear to each other. Let  $\xi$ , P, v, and  $\xi'$ , P', v', represent the activity, pressure, and molecular volume of the ice and the water, respectively. From equation V,

$$d \ln \xi = \frac{v}{RT} dP$$
, and  $d \ln \xi' = \frac{v'}{RT} dP'$ .

In order to maintain equilibrium we must always keep  $\xi$  equal to  $\xi'$ . Hence,

 $d\xi = d\xi'$ , or  $d\ln \xi = d\ln \xi'$ .

Therefore the condition of continued equilibrium is,

$$\frac{v}{RT}dP = \frac{v'}{RT}dP' \text{ and } \frac{dP}{dP'} = \frac{v'}{v} \cdot$$

In order to maintain equilibrium the increments of pressure on the two phases must be inversely proportional to the molecular volumes.<sup>8</sup>

As a second illustration let us consider the same system of ice and water subject to a simultaneous change of pressure and temperature. The effect of increasing the pressure equally on both phases is to increase the activity of the ice more than that of the water. An increase of temperature has the same effect. By increasing the pressure and at the same time lowering the temperature, equilibrium may be maintained. The condition of equilibrium, as in the preceding case, is,

$$d \ln \xi = d \ln \xi'$$
,

but in this case the change in  $\xi$  and in  $\xi'$  is due in part to change in temperature, in part to change in pressure, that is,

<sup>8</sup> For a proof of this equation by other methods, see Lewis, Z. physik. Chem., 35, 343 (1900); These Proceedings, 36, 145 (1900).

$$d\ln \xi = \left(\frac{\partial \ln \xi}{\partial T}\right)_P dT + \left(\frac{\partial \ln \xi}{\partial P}\right)_T dP,$$

and

$$d\ln \xi^I = \left(\frac{\partial \ln \xi^I}{\partial T}\right)_P dT + \left(\frac{\partial \ln \xi^I}{\partial P}\right)_T dP.$$

Equating the second members of these equations and substituting for the partial differential coefficient their values from equations V and VIII.

$$\frac{Y - Pr}{RT^2}dT + \frac{v}{RT}dP = \frac{Y' - Pv'}{RT^2}dT + \frac{v'}{RT}dP,$$

or

$$\frac{Y - Pv - Y' + Pv'}{RT^2} dT = \frac{v' - v}{RT} dP.$$

The numerator of the first fraction is obviously equal to the heat of fusion of one mol of ice. Calling this Q, we have

$$\frac{dT}{dP} = \frac{(v' - v) T}{Q},$$

which is the familiar equation of Thomson for the change of freezing point with the pressure.

As a third illustration of the application of these equations we will consider a general method for determining the numerical value of the activity of a substance. Let us first consider a gas which is at such a pressure as no longer to obey the gas law. According to equation V we may write, for the influence of pressure on the activity, at constant temperature,

$$d\ln \xi = \frac{v}{RT}dP.$$

From this equation we may find the activity at one pressure when it is known at any other, if we know the molecular volume, v, as a function of the pressure, P. For this purpose we may use any empirical equation, such as that of van der Waals, namely,

$$P = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Differentiating this equation, substituting the value of dP in the preceding equation, and integrating between v and v', we obtain the equation,

$$\ln\left[\xi\left(v-b\right)\right] - \ln\left[\xi^{\prime}\left(v^{\prime}-b\right)\right] = \frac{b}{v-b} - \frac{b}{v^{\prime}-b} - \frac{2\,a}{R\,Tv} + \frac{2\,a}{R\,Tv^{\prime}}.$$

From this equation, assuming that the van der Waals formula is true and that the constants a and b are known for a given substance, the activity of that substance can be found at the volume v when it is known at any other volume, v'. At infinite volume the activity of the gas, by definition, is equal to its concentration, which is the reciprocal of its molecular volume. It is evident, therefore, that if in the above equation v' approaches infinity,  $\xi'$  approaches  $\frac{1}{v'}$  or  $\frac{1}{v'-b'}$  and the second, fourth, and sixth terms in the equation approach zero. Omitting these terms, therefore, and rearranging slightly, we have,

$$\ln \xi = \frac{b}{v - b} - \frac{2\alpha}{RTv} - \ln (v - b).$$

From this equation  $\xi$  can be found for any gas at any volume, v, provided the formula of van der Waals holds, and the values of a and b are known. Similarly any other empirical equation of condition may be used.

According to Amagat's experiments upon carbon dioxide at  $60^{\circ}$  the molecular volumes of this gas at 50, 100, 200, and 300 atmospheres, are, respectively, 0.439, 0.147, 0.0605, and 0.0527 liters. From these data I have calculated the values of a and b at this temperature and found,

$$a = 3.1$$
;  $b = 0.034$ 

(pressure being expressed in atmospheres, volume in liters, and R consequently having the value 0.0820).

Substituting these values in the above equations, we obtain the values for the activity of carbon dioxide at 60° given in the following table:

| P.    | е.   | ξ.  | ξ,c. |
|-------|------|-----|------|
| 50    | 2.3  | 1.6 | 0.70 |
| 100   | 6.8  | 2.6 | 0.38 |
| 200 . | 16.5 | 3.2 | 0.19 |
| 300   | 19.0 | 4.2 | 0 22 |

The first column gives the pressure, the second gives the concentration in mols per liter  $\left(\frac{1}{v}\right)$ , the third gives the activity, also in mols per liter, and the fourth gives the ratio of activity to concentration, which for a perfect gas is always unity. The increase in this quotient between 200 and 300 atmospheres is interesting, and the whole table shows how little either the pressure or the concentration of a compressed gas is suited to act as a measure of the escaping tendency.

If instead of determining the activity of gaseous carbon dioxide we desired to determine that of CO<sub>2</sub> in some other phase, for example in a solution of sodium bicarbonate in water at a given temperature and concentration, it would be only necessary to know the pressure or the concentration of carbon dioxide gas in equilibrium with that phase. For the activity there would be the same as in the gas, and the latter could be determined by the above method.

This, therefore, is a perfectly general method for determining the numerical value of the activity. However, it is to be emphasized that in most cases where the conception of activity is useful, it is not necessary to know the numerical value, but only the ratio of the activities in two given states. This will be illustrated in another section.

Influence of Pressure, Temperature, and Concentration upon the Activity of the Constituents of a Binary Mixture.

The equations in this section will apply not only to a homogeneous liquid mixture, but also to a gaseous mixture, or solid solution, in fact

to any homogeneous phase whatever which is composed of the two molecular species,  $X_1$  and  $X_2$ . The composition of a binary mixture we shall express, following Ostwald, by the molecular fractions (Molenbruche),  $N_1$  and  $N_2$ , so defined that  $N_1 + N_2 = 1$ . By one mol of the mixture we shall mean that amount which contains  $N_1$  mols of

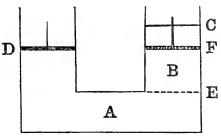


FIGURE 1.

 $X_1$  and  $N_2$  of  $X_2$ . Later, in dealing with mixtures of more than two constituents, the fractions  $N_1$ ,  $N_2$ ,  $N_3$ , etc., will be similarly defined, so that  $N_1 + N_2 + N_3 + \ldots = 1$ .

The influence of pressure upon the activity of either constituent of

a binary mixture may be found by means of the apparatus shown in Figure 1. A contains the mixture of  $X_1$  and  $X_2$ . D is a piston which determines the pressure on A. E is a membrane permeable only to  $X_1$ . B contains a solution of  $X_1$  in its ideal solvent. F is a piston permeable only to the latter. Above F is the pure solvent.

The pressure on the piston F is the osmotic pressure,  $\Pi$ , of the ideal solution in B. In general if the pressure, P, on D is changed, the equilibrium will be disturbed and the substance  $X_1$  will pass through E, unless at the same time the pressure on F is changed by a suitable amount. Let us find the mathematical expression for the change in  $\Pi$ , which just compensates a given change in P.

Starting with the piston F at E and with a large (better, an infinite) amount of the mixture in A, occupying the volume V, let us perform isothermally the following cycle of reversible operations.

(1) Keeping the pressure P constant on the piston D, and keeping the pressure on F also constant and equal to the corresponding osmotic pressure,  $\Pi$ , raise F until one mol of  $X_1$  passes into B, where it occupies the volume v'. The diminution in the volume of A we will denote by the symbol  $\overline{v}$ . The work done by the system by means of the pistons F and D is, therefore,

$$A_1 = \Pi v' - P\overline{v}$$
.

(2) Now increase the pressure on the piston D to P + dP, and at the same time increase the pressure on F to  $\Pi + d\Pi$ ,  $d\Pi$  being the increment in  $\Pi$  which is necessary to prevent  $X_1$  from passing in either direction through E. The volume of A will change from  $V - \bar{v}$  to  $(V - dV) - (\bar{v} - d\bar{v})$ , and the volume of the solution will change from v' to v' - dv'. The work done by the system by means of the pistons F and D is,

$$A_2 = - \operatorname{\Pi} dv' - P \left( d \operatorname{V} - d \widetilde{v} \right).$$

(3) Keeping the pressures on the two pistons constant and equal to  $\Pi + d\Pi$  and P + dP respectively, lower F to E, forcing the mol of  $X_1$  back into  $\Lambda$ . The work done by the two pistons is

$$A_3 = - (\Pi + d\Pi)(v' - dv') + (P + dP)(\bar{v} - d\bar{v}).$$

(4) Change the pressure in A back to P. The piston F is stationary, and the work done by the piston D is,

$$A_4 = PdV$$
.

The surface C does not change its position during these operations (according to the definition of the ideal solvent). The total work done by the system is therefore equal to the sum of  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$ , and since the cycle is isothermal and reversible this sum is equal to zero, by the second law of thermodynamics. Equating the terms to zero and simplifying gives,

$$\bar{v}dP - v'd\Pi = 0.$$

v', the molecular volume in the ideal solution, is equal to  $\frac{RT}{\Pi}$ . Substituting this value in the last equation gives,

$$\frac{d \ln \Pi}{dP} = \frac{\bar{v}}{RT}.$$

The activity of  $X_1$ ,  $\xi$ , is the same in the mixture A and the solution B and its value in terms of H is given by equation III. Substituting for H and expressing in the equation the constancy of temperature and composition, we have,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_{T, \, X} = \frac{\bar{r}}{R \, T}.\tag{IX}$$

This is the general equation for the influence of pressure upon the activity of one constituent of a binary mixture. The quantity  $\bar{v}$  is of very great importance in the thermodynamics of mixtures. It is the increase in volume of an infinite quantity of a mixture when one mol of the constituent in question is added to it. We will call  $\bar{v}$  the partial molecular volume of that constituent.

Similarly we may define the partial molecular energy, entropy, etc., and these quantities play the same rôle in the thermodynamics of mixtures that the molecular volume, energy, entropy, etc., do in the treatment of pure substances.

An important difference between the partial molecular volume in a mixture and the molecular volume of a pure substance is that while the latter is always positive the former need not be. Therefore the activity of one of the constituents of a mixture may either be increased or diminished by increase of pressure on the mixture.

 $<sup>^9</sup>$  We will use the subscript N with the partial differential coefficient to denote constancy of composition in the mixture.

If a mixture contains  $X_1$  and  $X_2$  in the proportion of  $N_1$  mols of the former to  $N_2$  of the latter, the relation of the partial molecular volumes,  $\overline{r}_1$  and  $\overline{r}_2$  is readily seen. If we add to an infinite quantity of the mixture  $N_1$  mols of  $X_1$ , the mixture will increase in volume by  $N_1\overline{r}_1$ . Then adding  $N_2$  mols of  $X_2$  the volume increases by  $N_2r_2$ . Altogether we have done nothing more than add one mol more of the original mixture. The total change of volume must therefore equal v, the volume of one mol of the mixture. Hence,

$$N_1 \overline{v_1} + N_2 \overline{v_2} = v.$$
 X

From equation IX we have the following two equations for the two constituents:

$$\left(\frac{N_1 \partial \ln \xi_1}{\partial P}\right)_{T,N} = \frac{N_1 \overline{v}_1}{RT},$$

$$\left(\frac{N_2 \partial \ln \xi_2}{\partial P}\right)_{T, N} = \frac{N_2 \bar{r}_2}{RT}$$

Adding these two, we obtain the important equation,

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial P}\right)_{T, N} = \frac{v}{RT}^{10}$$
 XI

The influence of temperature upon the activity of one of the constituents of a mixture may also be determined with the aid of the apparatus of Figure 1. Starting with the piston F at E, we may perform the following cycle of reversible operations, keeping the pressure constant upon both D and C.

- (1) At the temperature T raise the piston F until 1 mol of  $X_1$  passes into B, where it occupies the volume v'. The pressure on F is kept at such a pressure,  $\Pi$ , that the activity of  $X_1$  is always the same in B as in A.
- (2) Lower the temperature to T dT, moving the piston F so that none of  $X_1$  passes through E. The volume of B is changed to v' dv' and the osmotic pressure to  $\Pi d\Pi$ .

$$N_1 \left(\frac{\partial \ln \xi_1}{\partial P}\right)_{T, N} + N_2 \left(\frac{\partial \ln \xi_1}{\partial P}\right)_{T, N} = \frac{v}{RT},$$

in order to emphasize the peculiar significance of the term  $N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2$ . In general we shall see that the equations of a mixture may be obtained from those of a pure substance by substituting this series of terms in place of  $\partial \ln \xi$ .

<sup>10</sup> The equation is written in this form rather than in the more conventional form,

(3) Lower F once more to E, under the constant pressure  $\Pi - d\Pi$ .

(4) Raise the temperature to T.

The total work done by the pistons D and C is zero, since they are under constant pressure and finally return to their original positions. The whole work done by the system is, therefore, the work done by the piston F. This is obviously the sum of the following four terms:

$$A_1 = \Pi v',$$
  
 $A_2 = -\Pi dv',$   
 $A_3 = -(\Pi - d\Pi)(v' - dv'),$   
 $A_4 = 0.$ 

The sum of these terms, neglecting the differential of the second order, is  $r'd\Pi$ . This is the total work done by the system during the cycle, and therefore from the second law of thermodynamics,

$$v'd\Pi = \frac{Q}{T}dT,$$

where Q is the heat absorbed in process (1). Q is the sum of three terms. The first is the increase in internal energy when one mol of  $X_1$  passes from A to B, which we may call  $U_{(XII)}$ . The second is the osmotic work,  $\Pi v'$ , which is equal to RT. The third is the work done by the pressure P acting on piston D, which is equal to  $P\overline{v}$  where  $\overline{v}$  is the partial molecular volume of  $X_1$  as before. Hence,

$$\begin{split} v'\frac{d\Pi}{dT} &= \frac{I'_{\text{XIII}} + RT - P\overline{v}}{T} \cdot \\ v' &= \frac{RT}{\Pi} \, , \end{split}$$

Now

and therefore

$$\frac{d \ln \Pi}{dT} = \frac{U_{(\text{XII})} + RT - P \overline{v}}{RT^2}.$$

Combining this equation with equations III and IV, as we did in deriving equation VIII, we have

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P,N} = \frac{U_{(\text{XII})} + U_{(\text{IV})} - P\bar{v}}{RT^2}.$$

The sum of  $U_{(XII)}$  and  $U_{(IV)}$  is the increase in internal energy when one mol of  $X_I$  passes from an infinite quantity of the mixture into a

state of infinitely attenuated vapor. We will denote this quantity by  $\overline{Y}$ . It bears the same relation to the value Y of a pure substance as the quantity  $\overline{c}$  does to c. We may call it the partial "ideal heat of evaporation."

The above equation then becomes,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P,N} = \frac{\bar{Y} - P\bar{v}}{RT^2},$$
 XII

which is a general equation for the influence of temperature upon the activity of one of the constituents of a mixture when the pressure and the composition are constant.<sup>11</sup>

Just as equation X was proved we may show that for one mol of the mixture.

$$Y = N_1 \overline{Y}_1 + N_2 \overline{Y}_2.$$
 XIII

Hence we obtain an equation analogous to equation XI, namely

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial T}\right)_{P,N} = \frac{\Upsilon - Pr}{RT^2}.$$
 XIV

Here as before v is the volume occupied by one mol of the mixture and Y the increase in internal energy when one mol of the mixture is converted into infinitely attenuated vapor, or in other words when it evaporates in a vacuum.<sup>12</sup>

$$\left(\frac{\partial \ln p}{\partial T}\right)_{P,X} = \frac{\overline{Q}}{RT^2},$$

where  $\overline{Q}$  is the partial heat of vaporization (including the external work). This is in a simpler form than the equation obtained by Kirchhoff,

$$\left(\frac{\partial \ln \frac{p_0}{p}}{\partial T}\right)_{p,N} = \frac{\left(\frac{\partial Qx}{\partial x}\right)}{RT^2}$$

(see Nernst, Theoretische Chemie, 4 Edit., p. 118).

<sup>12</sup> Equation XII bears the same relation to XIV that the equation of Kirchhoff does to one obtained by Nernst, namely,

$$\frac{d \ln \frac{p_0}{p} + x d \ln \frac{p'_0}{p'}}{dT} = -\frac{Q(x)}{RT^2}$$

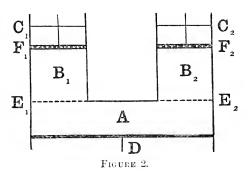
(Nernst Theor. Chem., 4 Edit, p. 117).

<sup>11</sup> The approximate equation for the vapor pressure of one constituent of a binary mixture obtained from equation XII is,

Finally we must determine how the activities of the components of a mixture vary when the composition is changed at constant temperature and pressure. In order to solve this problem we may employ the apparatus shown in Figure 2. A contains a mixture of  $X_1$  and  $X_2$ .  $E_1$  is a membrane permeable only to  $X_1$ ,  $E_2$  one permeable only to  $X_2$ . In  $B_1$  and  $B_2$  are ideal solutions of  $X_1$  and  $X_2$ . The two pure ideal solvents lie above the pistons,  $F_1$  and  $F_2$ , which are permeable only to these solvents. D is a piston which exerts a constant pressure on A. The pressure at  $C_1$  and  $C_2$  will also be held constant. We may perform the following isothermal cycle of reversible operations, starting with  $N_1$  mols of  $X_1$  and  $N_2$  mols of  $X_2$  in A, and none of these substances in  $B_1$  and  $B_2$ , the pistons  $F_1$  and  $F_2$  being at  $E_1$  and  $E_2$ .

(1) Keeping the pressures on  $F_1$  and  $F_2$  constant and at such values,  $\Pi_1$  and  $\Pi_2$ , as to maintain equilibrium with the mixture in A, raise

these two pistons at such rates that as  $X_1$  and  $X_2$  pass into  $B_1$  and  $B_2$  the remaining mixture in A still keeps its original composition. Finally, when all the mixture has disappeared from A there will be  $N_1$  mols of  $X_1$  in  $B_1$  where it exerts the osmotic pressure  $\Pi_1$ , and occupies a volume which we will call  $V_1$ , and there will be  $N_2$  mols of  $X_2$  in  $B_2$ 



be  $N_2$  mols of  $X_2$  in  $B_2$  the osmotic pressure being  $\Pi_2$  and the volume  $V_2$ .

- (2) By simultaneous movements of the pistons  $F_1$  and  $F_2$  change the volumes in  $B_1$  and  $B_2$  to  $V_1 dV_1$  and  $V_2 dV_2$ . The osmotic pressures will change to  $\Pi_1 + d\Pi_1$  and  $\Pi_2 + d\Pi_2$ . The solutions in  $B_1$  and  $B_2$  are now able to exist in equilibrium, not with the original mixture, but with a mixture containing  $X_1$  and  $X_2$  in another proportion, say  $N_1$  mols to  $N_2 dN_2$  mols.
- (3) Form a mixture of this composition in A by lowering the pistons  $F_1$  and  $F_2$ . This operation will be just the reverse of (1), except that  $X_1$  and  $X_2$  enter the mixture in the constant proportion, not of  $N_1$  to  $N_2$  but of  $N_1$  to  $N_2 dN_2$ . At the end of this process all of  $X_1$  and all but  $dN_2$  of  $X_2$  will have passed into A.
- (1) Finally force into A the remaining  $dN_2$  mols of  $X_2$ , whereby the whole system returns to its original condition.

The work done during this cycle at D, C<sub>1</sub>, and C<sub>2</sub>, is zero, since in each case the final position is the same as the initial, and the pressure is constant throughout the cycle. Therefore the total work done by the system during the cycle is that done by the pistons F<sub>1</sub> and F<sub>2</sub>, which is as follows:

In operation (1),

$$A_1 = \Pi_1 V_1 + \Pi_2 V_2$$

In operation (2),

$$A_2 = - \Pi_1 d V_1 - \Pi_2 d V_2.$$

In operations (3) and (4), except for a differential of the second order,

$$A_3 + A_4 = -(\Pi_1 + d\Pi_1)(V_1 - dV_1) - (\Pi_2 + d\Pi_2)(V_2 - dV_2).$$

By the second law of thermodynamics the sum of these terms, the total work of a reversible isothermal process, rust be zero. Hence, neglecting differentials of the second order,

$$V_1 d\Pi_1 + V_2 d\Pi_2 = 0.$$

Since we are dealing with ideal solutions,

$$V_1 = \frac{N_1 RT}{\Pi_1}$$
 and  $V_2 = \frac{N_2 RT}{\Pi_2}$ ,

hence

$$N_1 d \ln \Pi_1 + N_2 d \ln \Pi_2 = 0.$$

Now the activity  $\xi_1$  of  $X_1$  in A is always the same as in  $B_1$ , and  $\xi_2$  in A is the same as in  $B_2$ ; hence, applying equation III ( $\rho$  and T being constants) we have,

$$N_1 d \ln \xi_1 + N_2 d \ln \xi_2 = 0,$$
 XV

which may also be written

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial N_1}\right)_{P, T} = 0, \qquad XVA$$

or 
$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial N_2}\right)_{P, T} = 0, \quad XV B$$

It is not possible from thermodynamics alone to predict how the activity of each of the constituents of a binary mixture will change with a change in composition. But if the change in one of the activities is known, the change in the other may be found from the above simple relation.<sup>13</sup>

#### MIXTURES OF MORE THAN TWO COMPONENTS.

In the derivation of equations IX and XII no use was made of the provision that the mixture contained but two constituents, and these equations therefore show the effect of pressure and of temperature upon the activity of one of the constituents of a mixture of any number of constituents. In the same way that equations XI, XIV, and XV were found we may obtain the following equations:

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial P}\right)_{T,N} = \frac{v}{RT}, \quad \text{XVI}$$

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial T}\right)_{P,N} = \frac{Y - Pv}{RT^2}, \quad \text{XVII}$$

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{P,N} = 0. \quad \text{XVIII}$$

## DILUTE SOLUTIONS.

Equations XV and XVIII assume a very simple form when one of the constituents of a mixture is present in such small amount as to constitute a perfect solution. If a mixture consist of a very small amount of a substance  $X_1$  and a large amount of a substance  $X_2$ , we may call the latter the solvent and the former the solute. If the solute is extremely dilute, then, according to equation II, its activity  $\xi_1$  is proportional to its concentration and therefore to  $X_1$ . Hence,

$$d\ln \xi_1 = d\ln N_1,$$

and equation XV becomes,

$$N_2 d \ln \xi_2 = -dN_1, \qquad XIX^*$$

or 
$$d \ln \xi_2 = -\frac{dN_1}{N_2} \cdot \qquad XIX^{\#} A$$

<sup>13</sup> An approximate equation which is a special form of equation XV is Duhem's equation for the vapor pressures of a binary mixture, namely,  $N_1d \ln p_1 + N_2d \ln p_2 = 0$ . This equation is true only when the vapors obey the gas law. See Lewis, Journ. Amer. Chem. Soc., 28, 569 (1906).

This equation states that the relative lowering of the activity of a solvent by the addition of a small quantity of a solute is equal to the number of mols of solute divided by the number of mols of solvent.

This statement comprises in itself practically all the laws of dilute solutions. Raoult's law is a special but only approximate form of equation XIX, for equation XIX is true of every solution when infinitely dilute, but Raoult's law is not true even at infinite dilution, except when the vapor of the solvent is a perfect gas.

If the solute,  $X_1$ , is dissolved, not in a pure solvent, but in a mixture of  $X_2$ ,  $X_3$ , etc., then for the perfect dilute solution we find in place of equation XIX,

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \dots = -dN_1.$$
 XX\*

Some Applications of the Preceding Equations.

Equations I-XX can be combined in a very great variety of ways to give important results. A few examples, however, will suffice to show the manner in which these equations may be employed.

First, as a simple example, we may derive the formula for the lowering of the freezing point of a perfect solution. According to equation XIX, the activity of a pure liquid is always lowered by the addition of a solute. If therefore a liquid and solid are together at the freezing point and a solute is added to the liquid, the activity of the latter will become lower than that of the solid, and the solid will melt. On the other hand, if we start again with liquid and solid at the freezing point and lower the temperature, we see from equation VIII that the activity of the solid will decrease faster than that of the liquid and the liquid will disappear. It is obvious, therefore, that by adding a solute to a freezing mixture and at the same time lowering the temperature by a suitable amount, the equilibrium between solid and liquid can be maintained. The necessary condition for the maintenance of equilibrium is that the activity  $\mathcal{E}_2$  of the solvent  $X_2$  in the liquid state remain equal to the activity  $\mathcal{E}_2$  of  $X_2$  in the solid state. Hence,

$$d\ln \xi^{I}_{2} = d\ln \xi_{2}.$$

Now, assuming that the solid does not dissolve any of the solute, the change in activity of the solid  $X_2$  is due merely to change of temperature, and thus from equation VIII,

$$d\ln \xi'_2 = \frac{\Upsilon'_2 - Pr'_2}{RT^2} dT.$$

But the activity of the solvent in the liquid phase is changed both by the change in temperature and by the presence of  $dN_1$  mols of solute. That is,

$$d \ln \xi_2 = \left(\frac{\partial \ln \xi_2}{\partial T}\right) dT + \left(\frac{\partial \ln \xi_2}{\partial N_1}\right) dN_1.$$

Whence by means of equations XII and XIX

$$d \ln \xi_2 = \frac{\bar{Y}_2 - P\bar{v_2}}{RT^2} dT - \frac{dN_1}{N_2}.$$

Equating the second members of this equation and the one above,

$$\frac{\mathbf{Y'}_{2} - Pv'_{2}}{RT^{2}}dT = \frac{\bar{\mathbf{Y}}_{2} - P\bar{v}_{2}}{RT^{2}}dT - \frac{dN_{1}}{N_{2}},$$

or

$$-N_{2}\frac{dT}{dN_{1}} = \frac{RT^{2}}{Y_{2} - Pv_{2} - \bar{Y}_{2} + P\bar{v}_{2}}$$

But it is obvious on inspection that the denominator of the second member is merely the heat of fusion of one mol of solid, which we may call Q. If the solution is very dilute we may also simplify by writing  $N_2 = 1$ . Hence,

$$\frac{dT}{dN_1} = -\frac{RT^2}{Q}.$$

This is the familiar equation of van't Hoff for the lowering of the freezing point by a dissolved substance.

As a second example we may study the following system. A mixture of  $X_2$  and  $X_3$  in the molecular proportion of  $N_2$  to  $N_3$  are in equilibrium with a second phase consisting of pure  $X_2$ . Let us determine the change in activity of  $X_3$  when a small quantity  $dN_1$  of a substance  $X_1$  is dissolved in the mixture. At constant temperature and pressure the activity  $\xi'_2$  of the pure phase of  $X_2$  is a constant, and therefore the activity,  $\xi_2$ , of  $X_2$  in the mixture is also constant. Equation XX therefore becomes,

$$N_3 d \ln \xi_3 = -d N_1.$$
 XXI

This interesting equation has, I believe, not hitherto been obtained, even in an approximate form. Its meaning may be illustrated by the following example: If a saturated solution of salt in 1000 grams of water is in contact with solid salt, and 1 gram of sugar is added, then

the activity of the water is lowered by the same per cent as when 1 gram of sugar is added to 1000 grams of pure water.

An interesting system is one composed of two phases, both of which are mixtures of the same composition. An important example of such a system is a constant boiling mixture and its saturated vapor. Here  $N_2$ ,  $N_3$ , etc., which are the molecular fractions in the one phase, are equal respectively to  $N_2$ ,  $N_3$ , etc., in the other phase. If the conditions are changed by changing the temperature or pressure or by adding a third substance  $X_1$  to one or both of the phases, then equilibrium can only be maintained by keeping the activity of each component the same in both phases; thus we may write as usual,

$$d \ln \xi_2 = d \ln \xi'_2$$
,  $d \ln \xi_3 = d \ln \xi'_3$ ,

etc.; but since  $N_2 = N'_2$ , etc., we may write

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \cdots = N_2 d \ln \xi_2' + N_3' d \ln \xi_3' + \cdots$$

Now the first member of this equation represents a change which may be the resultant of the changes produced by change of temperature, change of pressure, and the addition of  $dN_1$  mols of the solute  $X_1$ . Each of these changes is represented alone by equations XVI, XVII, or XX. Therefore,

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial T}\right)_{P,N} dT = \frac{\Upsilon - Pv}{RT^2} dT,$$

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial P}\right)_{T,N} dP = \frac{v}{RT} dP,$$

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{T,P} dN_1 = -dN_1.$$

We may therefore write the sum of these as follows:

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \cdots = \frac{\Upsilon - Pv}{RT^2} dT + \frac{v}{RT} dP - dN_1.$$

Likewise we find

$$N'_{2}d\ln \xi'_{2} + N'_{3}d\ln \xi'_{3} + \cdots = \frac{Y' - Pv'}{RT^{2}}dT + \frac{v'}{RT}dP - dN'_{1},$$

where  $dN'_1$  is the number of mols of the solute in one mol of the second phase. Equating the second members of these two equations we have,

$$\frac{(Y - Pv) - (Y' - Pv')}{RT^2} dT + \frac{(v - v')}{RT} dP - dN_1 + dN_1 = 0.$$

The numerator of the first term, which we may call Q, is obviously the heat absorbed when a mol of the mixture passes from the first phase to the second, and (v - v') is the decrease in volume accompanying the same change. Thus,

$$\frac{Q}{RT^2}dT + \frac{v - v'}{RT}dP - dN_1 + dN_1' = 0.$$
 XXII\*

This extremely general equation shows how the variations in temperature, pressure, and quantity of solute must be regulated in order to maintain equilibrium in such a system. Several special cases are worthy of notice. If pressure and temperature are the only variables, in other words if  $dN_1$  and  $dN_1$  are zero, then the equation becomes,

$$\frac{dP}{dT} = \frac{Q}{(v' - v)T}$$

This equation is identical with the familiar Clapeyron-Clausius equation. It shows, for example, that the vapor pressure from a constant boiling mixture varies with the temperature in the same way that the vapor pressure of a pure substance does.

If in equation XXII, dP and  $dN'_1$  are zero, there remains an equation for the change in temperature which compensates for the addition of a solute soluble in one phase only, namely,

$$dT = \frac{RT^2}{O} dN_1.$$

Thus, for example, the boiling point of a constant boiling mixture is changed by the addition of a non-volatile solute according to the same law as that which applies in the case of a simple solvent. Q is of course the heat of vaporization of one mol of the mixture.

In the same way, by making dT equal to zero in equation XXII, a formula may be derived for the lowering of the vapor pressure of a constant boiling mixture when a solute is added at constant temperature.

<sup>14</sup> This equation I have already proved in a less rigorous way (Journ. Amer. Chem. Soc., 28, 766, 1906). It has considerable practical importance, as it increases the number of solvents in which molecular weights may be determined by the boiling point method.

If instead of the system considered above we study a system of the type represented by a mixture at its eutectic point, we may derive a set of equations, entirely similar to the above, which show the change of the eutectic temperature with the pressure, and the change of the eutectic temperature at constant pressure, or of the eutectic pressure at constant temperature, when a solute is added to the mixture.

These examples will suffice to show the way in which equations I-XX may be applied to the derivation of other thermodynamic equations.

### THE LAWS OF CHEMICAL EQUILIBRIUM.

Hitherto we have considered only those processes in which each molecular species persists without any change except that of passing from one phase to another. We will now consider those processes in which the molecular species react with each other to form new species, and it will be shown that the activity of a given species is not only a measure of the tendency of that species to escape into some other phase, but is also a perfect measure of the tendency of the species to take part in any chemical reaction. In other words, the activity is an exact measure of that which has been rather vaguely called the "active mass" of a substance.

Let us consider the reaction represented by the following equation,

$$aA + bB + \cdots \stackrel{\longleftarrow}{\Longrightarrow} oO + pP + \cdots$$

where a mols of the substance A, b mols of B, etc., combine to form o mols of O, p mols of P, etc. The several substances may exist in the pure state, or in mixtures; may be in one phase or in different phases, and there may be other substances present which take no part in the reaction. In other words, we are considering any system whatever in which a given chemical reaction occurs. Let us find the conditions for equilibrium in this reaction.

We may choose a liquid which is an ideal solvent for each of the substances taking part in the reaction. If this ideal solvent is brought in contact with the system through a membrane permeable only to the substances which take part in the reaction, these substances will enter the solvent, and when the system comes to a final condition there will be equilibrium in the chemical reaction, both in the original system and in the ideal solution. Moreover, the activity of each of the molecular species must be the same throughout the original mixture and in the ideal solution.

Now in the ideal solution it is easy to show rigorously, as van't Hoff has done, that the condition of equilibrium at a given temperature is,

$$\frac{C_O^n C_P^n \cdot \cdot \cdot}{C_A^n C_B^n \cdot \cdot \cdot} = \text{constant.}$$

where  $C_A$ , etc., represent the concentrations. But in this solution the concentrations are proportional to the activities, and therefore,

$$\frac{\xi_{0}^{o/p}, \dots}{\xi_{1}^{o/p}, \dots} = K.$$
 XXIII

where K is another constant. Since the activities  $\xi_A$ , etc., are not only the activities in the ideal solution, but also in the original system, it is obvious that equation XXIII expresses a law of extraordinary generality.

The above quotient, which we have called K, has a value which, for a given reaction at a given temperature, does not depend upon the medium in which the reaction occurs, nor upon the concentrations, nor upon the pressure, nor upon the nature or number of the phases which are concerned in the reaction. In other words K depends only upon the temperature and the specific nature of the reaction. It is therefore a better measure of the true "affinity" of a chemical reaction than any quantity that has hitherto been used for this purpose.

The equilibrium ratio, K, changes with the temperature according to a simple law. We may imagine the substances taking part in a given reaction all vaporized in a space so large that each vapor behaves like a perfect gas. If the reaction reaches equilibrium under these conditions, it is easy to show that the following equation of van't Hoff is entirely exact, namely,

$$\frac{d\ln\frac{C_0^*C_P^*\cdots}{C_A^*C_B^*\cdots}}{dT} = \frac{\mathfrak{U}}{RT^2},$$

where  $C_A$ ,  $C_B$ , etc., represented the concentrations, and II is the increase in internal energy when the reaction occurs in this extremely attenuated gaseous phase.

Since we are dealing with infinitely attenuated vapors,  $C_A$ , etc., may be replaced by  $\xi_A$ , etc., whence

$$\frac{d\ln K}{dT} = \frac{11}{RT^2}.$$
 XXIV

Since at constant temperature K is independent of the conditions under which a reaction occurs, it is obvious that the change with the temperature of the equilibrium ratio of the reaction in any system whatever is given in equation XXIV. The important quantity ll, the heat of reaction in the dilute gaseous phase, is equal to the heat of reaction in any other condition less the algebraic sum, for all the substances taking part in the reaction, of the quantities which we have denoted by the symbol Y.

The importance of this quantity ll has been recognized by Berthelot, who wrote in 1875, 15 "J'ai défini spécialement la chaleur de combinaison atomique, laquelle exprime le travail réel des forces chimique, et doit être rapportée à la réaction des gaz parfaits, opérée à volume constant."

The following interesting example will serve to illustrate the simultaneous application of equation XXIII or XXIV with the preceding equations. Let us prove the theorem first demonstrated by Stortenbeker, <sup>16</sup> namely, that the freezing point of a substance like  $\operatorname{CaCl}_2 \cdot \operatorname{6H}_2\operatorname{O}$  which partly dissociates in the liquid phase, is not changed by the addition to the liquid of a small quantity of either of the products of dissociation ( $\operatorname{CaCl}_2$  or  $\operatorname{H}_2\operatorname{O}$ ). When the solid,  $\operatorname{CaCl}_2 \cdot \operatorname{6H}_2\operatorname{O}$ , melts, there are in the liquid  $N_1$  mols of  $\operatorname{CaCl}_2 \cdot \operatorname{6H}_2\operatorname{O}$ , to  $N_2$  mols of  $\operatorname{CaCl}_2$  and  $N_3$  mols of  $\operatorname{H}_2\operatorname{O}$ , where  $N_3 = \operatorname{6}N_2$ . Let us find the effect produced by adding  $dN_3$  mols of  $\operatorname{H}_2\operatorname{O}$  at constant temperature and pressure. According to equation XVIII,

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + N_2 \partial \ln \xi_3}{\partial N_3}\right)_{P, T} = 0.$$

From this equation, since  $N_3 = 6 N_2$ , it is obvious that,

$$N_1 d \ln \xi_1 + N_2 (d \ln \xi_2 + 6 d \ln \xi_3) = 0.$$

Now since the CaCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, and H<sub>2</sub>O are in equilibrium, equation XXIII states that,

$$\frac{\xi_2^{\xi_6}}{\xi_1} = K.$$

Taking the logarithm of both members and differentiating we have,

$$d \ln \xi_2 + 6 d \ln \xi_3 = d \ln \xi_1$$
.

<sup>&</sup>lt;sup>15</sup> Ann. Chim. Phys., 4, 1 (1875).

<sup>&</sup>lt;sup>16</sup> Zeit. phys. Chem., **10**, 183 (1892).

Combining this equation with the above gives,

$$N_1 d \ln \xi_1 + N_2 d \ln \xi_1 = 0$$
, or  $d \ln \xi_1 = 0$ .

That is, the activity of the  $CaCl_2 \cdot 6$   $H_2O$  in the liquid phase is not changed by the addition of a small quantity of water, and it will therefore remain in equilibrium with the solid  $CaCl_2 \cdot 6$   $H_2O$  without change in the freezing point.

This example illustrates the general manner of treatment of systems in which molecular species may change through dissociation, association,

or through the mutual reaction of two or more species.

A little consideration of the simultaneous use of equations XXIII and XXIV with the preceding equations shows why it is that such equations as V and VIII hold for the activity of a molecular species such as  $H_2O$ , in a given pure phase, regardless of whether this phase is really composed entirely of the species  $H_2O$  or in part also of others such as  $(H_2O)_2$ ,  $(H_2O)_3$ ,  $(H^+ + OH^-)$ , etc., provided always that these other species can be formed from, and are in equilibrium with, the molecular species  $H_2O$ .

It may seem, at first sight, that equations XXIII and XXIV, as well as the preceding equations, while entirely exact and general in their scope, may not be readily applied to certain concrete problems where the value of the activity cannot be obtained from existing data. As a matter of fact, however, it is seldom important to know the numerical value of the activity in any one state, but rather the ratio between the activity of a substance in one state and that in another, and this ratio may be obtained in a variety of ways.

In fact one of the most important problems to which the equations derived in this paper may be applied, concerns the dissociation of salts in aqueous solutions into their ions, although from the nature of the ions we are never able to determine the numerical values of their activities. Let us consider the dissociation of such a substance as hydrochloric acid in aqueous solution, according to the reaction,

$$HCl = H^+ + Cl^-$$
.

According to the ordinary mass law,

$$\frac{\mathrm{C_{H}C_{Cl}}}{\mathrm{C_{HCl}}} = K.$$

Now this equation has been shown to be false, if we calculate the concentration of the ions from conductivity data. In all probability

this calculation is correct for solutions more dilute than tenth normal, <sup>17</sup> at least we may say that the conductivity data furnish the only means we have at present for calculating the ion concentrations. Every other method which has been employed measures not the concentrations, but the activities of the ions.

According to equation XXIII the activities of the undissociated acid and the ions are connected by the equation,

$$\frac{\xi_{\rm H}^{\xi_{\rm Cl}}}{\xi_{\rm HCl}} = K.$$

If therefore the mass law is false, it must be because the activity is not simply proportional to the concentration for one or more of these three substances. The problem, therefore, is to determine how the activity of the undissociated substance and the activity of the ions vary with the concentrations of both. It seems that all the facts which are at present known concerning electrolytic dissociation can be explained by the assumption that the ions are normal in their behavior; in other words, that the activity of each ion is simply proportional to its concentration, but that the undissociated portion of a strong electrolyte is abnormal in its behavior, the activity being proportional to the concentration of the undissociated substance multiplied by a quantity which depends solely on the total ion concentration, and increases with the latter. <sup>18</sup>

This simple statement suffices to explain qualitatively all the known anomalies of strong electrolytes. The exact quantitative formulation of this principle can hardly be made until still more experimental work has been done.

However, these considerations illustrate the method of treating chemical equilibrium when the ordinary mass law fails; in other words, when for one or more of the reacting substances the activity is not proportional to its concentration. For a complete analysis of such a case it is necessary to know how the activity of each of the reacting substances changes with its concentration and with the concentration of the other substances present.

<sup>&</sup>lt;sup>17</sup> The data upon which this paragraph is based are chiefly those contained in the very complete and instructive summary by Λ. Λ. Noyes, entitled, "The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory." (Technology Quarterly, 17, 293, 1904).

<sup>&</sup>lt;sup>18</sup> Probably, strictly speaking, the activity of the ions is likewise a function of the concentration of the undissociated substance, decreasing as the latter increases; but since the concentration of the undissociated substance always is very small in dilute solutions of strong electrolytes, its influence on the activity of the ions is therefore of minor importance.

THE RELATION OF ACTIVITY TO FREE ENERGY AND THERMODYNAMIC POTENTIAL.

It is interesting to see what relation the activity bears to certain other quantities which have been previously used for a similar purpose, especially the free energy of Helmholtz, which is itself intimately related to the various thermodynamic potentials.

The diminution in free energy which accompanies a given isothermal process, that is, the maximum work which the process may accomplish, is not a definite quantity until we define not only the process but also the system which is to be considered. To illustrate, we may consider a cylinder containing liquid and vapor, and a piston operated on by a spring which exerts a force exactly balancing the vapor pressure. When the piston moves out an infinitesimal distance, the decrease in free energy of the water and vapor is equal to pdV, but on the other hand the free energy of the spring increases by pdV, so that the free energy of the system comprising water, vapor, and spring does not change. In general we shall depart from the most common usage and consider the larger system, and we may therefore define the diminution in free energy of a given isothermal process as the maximum work which the process is able to accomplish, exclusive of the work done against the external pressure or pressures. The negative of this quantity, the increase in free energy, we shall denote by  $\Delta \tilde{g}$ . In a system whose properties are determined when the temperature, the pressure, and the compositions of the various phases are fixed, the general condition of equilibrium is that,

$$\delta \tilde{\alpha} = 0.$$

Let us now consider the change in free energy when one mol of a given molecular species passes from one state where its activity is  $\xi$ , to another state where its activity is  $\xi'$ . This change may be effected as follows: (1) Pass one mol reversibly from the first state into an ideal solvent. The solution will have the osmotic pressure  $\Pi$  and the volume v. (2) Change the concentration reversibly until the volume becomes v' and the osmotic pressure reaches such a value,  $\Pi'$ , that the

 $W_{\rm max}$  is the total work obtainable in the process in which system I, comprising one portion of volume  $V_2$ , at pressure  $P_1$ , another of volume  $V_2$ , at pressure  $P_2$ , etc., passes over into system II, comprising one portion of volume  $V_2$ , at pressure  $P_2$ , another of volume  $V_2$ , at pressure  $P_2$ , etc. The free energy as thus defined is identical with the thermodynamic potential,  $\zeta$ , of Gibbs.

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The completely general definition of free energy is given by the equation,  $-\Delta \delta = W_{\text{max}} + P_1 V_1 + P'_1 V'_1 + \cdots + P_2 V_2 - P'_2 V'_2 - \cdots$ 

solution is now in equilibrium with the substance in the second state. (3) Let the substance pass reversibly out of the ideal solution into

In the first step  $\Delta_1 = - \Pi v$ . In the second, the second state.  $\Delta_{z\widetilde{\mathcal{Y}}} = RT \ln \frac{\Pi'}{\Pi}$ . In the third,  $\Delta_{z}\widetilde{\mathcal{Y}} = \Pi'v'$ . Since by equation III the activities are proportional to the osmotic pressures in the ideal

solution, and since  $\Pi r = \Pi' r'$ , the total increase in free energy is,

$$\Delta \mathfrak{F} = RT \ln \frac{\xi'}{\xi} \cdot XXV$$

This is a general equation for the change in free energy in the passage of one mol of a given species from one state to another when the species itself does not change.<sup>20</sup> When we are dealing with the most general case of chemical reaction, when a mols of A, b mols of B, etc., combine to form o mols of O, p mols of P, etc., the total change in free energy will obviously be equal to that which accompanies the transfer of the factors of the reaction from the original system to another system where there is equilibrium, and the transfer of the products from this equilibrium system to the original system. By a combination, therefore, of equations XXIII and XXV, we find,

$$\Delta_{\widetilde{C}} = RT \ln \frac{\xi_{\mathcal{O}_{\varepsilon}^{\delta}p} \cdot \cdot \cdot}{\xi_{\mathcal{C}_{\varepsilon}^{\delta}p} \cdot \cdot \cdot} - RT \ln K.$$
 XXVI

Here  $\Delta_{\widetilde{K}}$  is the increase in free energy in any reaction when  $\xi_A$ ,  $\xi_B$ , etc., are the activities of the factors,  $\xi_0$ ,  $\xi_{P_0}$  etc., those of the products, and K is the equilibrium ratio.

# ELECTROMOTIVE FORCE EQUATIONS.

The change of free energy of a reversible galvanic cell is a direct measure of the electrical work of the cell. If E is the electromotive force of the cell, and F is the Faraday equivalent, then,

$$\Delta \mathfrak{F} = -mFE$$

where m is the number of Faraday equivalents which pass through the cell during the reaction in question, and in the direction in which the electromotive force E tends to send the current.

<sup>&</sup>lt;sup>20</sup> It would have been possible at the beginning to define the activity by means of this equation, and this would have led to a development of our set of equations, which from a mathematical standpoint would have been simpler than the one here adopted.

This value of  $\Delta \tilde{g}$  may now be substituted in equations XXV and XXVI. The former gives a formula for the electromotive force when only one substance takes part in the electrolytic process, as in certain concentration cells. The latter gives a general equation for any reversible cell whatever. These are,

$$E = \frac{RT}{mF} \ln \frac{\xi}{\xi'},$$
 XXVII

$$E = \frac{RT}{mF} \ln K - \frac{RT}{mF} \ln \frac{\xi_o^o \xi_p^p}{\xi_A^a \xi_b^a} \cdot XXVIII$$

In XXVII, m is the number of Faraday equivalents accompanying the passage of one mol; in XXVIII, it is the number accompanying the disappearance of a mols of A, b mols of B, etc.

One application of equation XXVII is of special interest. We may take it for granted that whenever two phases are in contact and a given molecular species is present in one of them, it will be present to some extent in the other. For example, if a rod of metallic silver dips into a solution of silver nitrate, we may suppose that silver ions are present not only in the solution, but also in the metal. The process which takes place at this electrode during the passage of a current may therefore be regarded as consisting in the passage of silver ions out of the electrode into the solution, or vice versa. Equation XXVII gives us, therefore, an expression for the single potential difference between an electrode and an electrolyte. If the ion in question is an elementary one (and monatomic) m is equal to v, the valence of the ion, and we may write equation XXVII in the following form,

$$E = \frac{RT}{v\dot{F}} \ln \frac{\xi_{M}}{\xi_{S}}$$
 XXIX

where E is the single potential difference,  $\xi_M$  is the activity of the ion in question in the electrode, and  $\xi_S$  is the activity of the same ion in the electrolyte. It is obvious that the quantity  $\xi_M$  is very similar to the electrolytic solution pressure of Nernst, but while the latter depends at a given temperature, not only upon the character of the electrode but also upon the nature of the medium in which the electrolyte is dissolved,  $\xi_M$  depends solely upon the character of the equation depends. Moreover, while equation XXIX is universally true, the equation of Nernst is obviously only true when the activity of the ion in the electrolyte is proportional to its concentration. We have in the application of equations XXIX (or XXVII) to the electromotive

force of concentration cells a remarkably useful means of determining, in the case of imperfect solutions, how the activity of a given molecular species varies with the concentration.

#### Summary.

It has been shown that a quantity named the activity, and closely related to the fugacity of the preceding paper, may be so defined that it serves as an ideal measure of the tendency of a given molecular species to escape from the condition in which it is. With the aid of this quantity a series of equations has been obtained, which have the same form as the approximate equations now in common use, but which are perfectly exact and general. The utility of these equations has been illustrated by their application to a number of special problems. From each equation two approximate equations can be immediately obtained, one for the vapor pressure of a substance, the other for its solubility. From equations XXIII, and following, important approximate equations are obtained by substituting concentrations for activities. The most general of the equations are collected for reference in the following list:

For a pure substance,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_T = \frac{v}{RT},\tag{V}$$

$$\left(\frac{\hat{c}\ln\xi}{\hat{c}T}\right)_{P} = \frac{Y - Pr}{RT^{2}}.$$
 VIII

For one constituent of a mixture,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_{T,N} = \frac{\overline{c}}{RT}, \qquad IX$$

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P,N} = \frac{\bar{Y} - P\bar{v}}{RT^2}.$$
 XII

For all the constituents of a mixture,

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + \cdots}{\partial P}\right)_{T,N} = \frac{r}{RT}, \qquad XVI$$

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + \cdots}{\partial T}\right)_{P,N} = \frac{Y - Pv}{RT^2}, \quad XVII$$

$$\left(\frac{N_1 \hat{\epsilon} \ln \xi_1 + N_2 \hat{\epsilon} \ln \xi_2 + \cdots}{\hat{\epsilon} N_1}\right)_{P, T} = 0.$$
 XVIII

For a perfect dilute solution,

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{P, T} = -1.$$
 XX\*

For the most general case of chemical equilibrium at a given temperature,

$$\frac{\xi_0^{o,p} \cdot \cdot \cdot}{\xi_1^{o,p} \cdot \cdot \cdot} = K \text{ (a constant)}.$$
 XXIII

For the change in the equilibrium ratio of any reaction with the temperature,

$$\frac{d\ln K}{dT} = \frac{11}{RT^2}.$$
 XXIV

For the increase in free energy when one mol of a given substance passes from one state to another,

$$\Delta_{\widetilde{\mathfrak{G}}} = RT \ln \frac{\xi'}{\xi}.$$
 XXV

For the increase in free energy in any chemical reaction,

$$\Delta_{\widetilde{\mathcal{S}}} = RT \ln \frac{\xi_{\alpha,p}^{\phi,p} \cdots}{\xi_{\alpha}^{\rho} \xi_{\alpha}^{\phi} \cdots} - RT \ln K.$$
 XXVI

For the electromotive force of any reversible cell,

$$E = \frac{RT}{mF} \ln K - \frac{RT}{mF} \ln \frac{\xi_o \xi_p^b \cdots}{\xi_A^a \xi_B^b \cdots}$$
 XXVIII

For the single potential at any electrode,

$$E = \frac{RT}{rF} \ln \frac{\xi_{\scriptscriptstyle M}}{\xi_{\scriptscriptstyle S}}.$$
 XXIX







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# CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE QUANTITATIVE DETERMINATION OF ARSENIC BY THE GUTZEIT METHOD.

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.

WITH TWO PLATES.



# THE QUANTITATIVE DETERMINATION OF ARSENIC BY THE GUTZEIT METHOD.

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.

Several attempts have been made to apply the so-called Gutzeit reactions to the quantitative determination of arsenic, especially in England since the epidemic in 1900 of arsenical poisoning from beer.

Kelynack and Kirkby¹ suggested that an approximate valuation of the amount of arsenic in a sample of beer may be made by comparing the stain produced on mercuric chloride paper by the arsenical hydrogen from a given portion of the sample with that produced by a definite quantity of a standard solution of arsenic.

Bird <sup>2</sup> made a careful study of the conditions under which the arsenical stain on mercuric chloride paper may be best obtained and identified, with especial reference to the interference of the hydrides of sulphur, phosphorus, and antimony. Although his work is extremely suggestive of a quantitative application, he himself considers that the test is only approximately quantitative, in that the stain obtained from a given amount of substance, say beer, may be shown to be greater or less than the stain representing a fixed limit of arsenic for that amount. He also regards it as a true negative test.

Treadwell and Comment <sup>3</sup> compared the stain obtained from the action of arsine on argentic nitrate paper with a series of stains from definite quantities of a standard solution of arsenic. The method, applied by these authors to the detection of arsenic in mineral waters, is said to have given good results.

Dowzard, <sup>4</sup> after describing a modification of the Gutzeit test which allows the detection of minute traces of arsenic in a small volume of solution, suggested the preparation of a standard set of stains, which should be kept in a tightly stoppered bottle in a dark place.

<sup>1</sup> Arsenical Poisoning in Beer Drinkers, p. 88. London, Ballière, Tindall, and Cox, 1901.

<sup>&</sup>lt;sup>2</sup> Analyst, 26, 181 (1901).

<sup>&</sup>lt;sup>3</sup> Treadwell, Kurzes Lehrbuch der Analytischen Chemie, 2, s. 138 (1902).

<sup>4</sup> Chem. News, **86**, 3 (1902).

Thomson 5 attempted to make the reaction quantitative by passing the arsenical hydrogen through a tube in which was hung a cotton thread or a paper, saturated with mercuric chloride solution, which, from the intensity of the stain produced upon it, should show the amount of arsenic present. Thomson states, however, that his results were untrustworthy.

Goode and Perkin 6 made a series of experiments to ascertain if the Gutzeit test could be made quantitative, and if a set of standards could be prepared which should be at least as permanent as the standard mirrors of the Berzelius-Marsh process. Stains were made as usual on paper treated with mercuric chloride, but the impossibility of making them permanent led to their abandonment for quantitative purposes, except that a given stain might be matched with freshly prepared standards.

Langmuir,<sup>7</sup> in order to detect the presence of undecomposed arsine in the Marsh test, placed in the end of the exit tube a slip of paper moistened with a saturated solution of mercuric chloride. It apparently did not occur to him that this might also be used quantitatively, but he seems to have employed the ordinary color stains successfully in the approximate analysis of glycerine for arsenic.

Aside from the above-quoted authors, there are doubtless many who have been able to use the Gutzeit reactions as a means of approximate analysis, but we have not met with a careful study of the conditions under which the reactions may be employed quantitatively with any degree of accuracy.

The chief difficulty in differentiating between stains caused by various amounts of arsine on either argentic nitrate or mercuric chloride paper lies in the fact that the action is partly over the surface and partly within the fibre of the paper. Further, a single layer of paper is not always sufficient to retain all the arsenic evolved, and stains from equal amounts of arsine may not always be of the same density. These difficulties disappear almost entirely if one allows the arsenical hydrogen to act not against, but along a surface. The principle, therefore, of the modification we suggest in order to make the Gutzeit reactions more accurately quantitative, is to allow the arsine to pass over a strip of paper impregnated with mercuric chloride and to compare the band of color thus obtained with a series of bands prepared from known amounts of a standard solution of arsenic. We think that

<sup>&</sup>lt;sup>5</sup> Royal Commission on Arsenical Poisoning, Final Report, **2**, 58. London, Eyre and Spottiswoode, 1903.

<sup>&</sup>lt;sup>6</sup> Jour. Soc. Chem. Ind., **25**, 507 (1906).

<sup>&</sup>lt;sup>7</sup> Jour. Amer. Chem. Soc., 21, 133 (1899).

the failure of Thomson to get good results was merely due to unsuitable conditions.

Our experience has not only confirmed the conclusion which has been reached by most of those who have investigated the Gutzeit reactions, that the use of mercuric chloride is preferable to that of argentic nitrate from a qualitative standpoint, but it has also shown that the former reagent is the one better suited to the quantitative analysis.

A careful study of the conditions of the reaction, following the principle stated above and made for the most part without knowledge of the work of the above-quoted authors, has shown that the reaction can be made the basis of a simple and fairly accurate quantitative method with no more than ordinary analytical precautions.

# THE METHOD.

Sensitized Mercuric Chloride Paper. For this purpose we used at first a smooth filter paper of close texture, but we have recently employed to greater advantage a cold pressed drawing paper made by Whatman. The latter not only gives better color results, but also, on account of its greater strength, withstands better any subsequent treatment for development or identification of the color. A square meter of this paper weighs about 160 grams (4 1-4 ounces per square yard). It is cut into strips having a uniform width of 4 mm., and we use for this purpose a carefully made brass rule of exactly this width. The cutting may be done with a sharp knife, but more accurately and in large quantity by the machine which should be accessible at any printing office.

The strips, which must be clean and free from dust, are sensitized by drawing them repeatedly through a five per cent solution of recrystallized mercuric chloride until they are thoroughly soaked. They are then placed to dry on a horizontal rack of glass rods or tubing, and, when dry, are at once cut into short lengths of 7 cm., discarding the ends by which the strips were held during the immersion. A bundle of these strips is placed in a stoppered tube or bottle containing calcic chloride covered by cotton wool, and is kept in the dark until needed.

The Reduction Apparatus. (See Figure A.) This consists of a glass bottle of 30 c.c. capacity, closed by a pure rubber stopper with two holes. Through one of these holes passes a small thistle tube, about 15 cm. long, reaching to the bottom of the bottle and constricted at its lower end to an opening of about 1 mm. The other hole carries an exit tube bent first at a right angle, then back again in the same

plane in the form of a  $\subset$ . To this is fastened by means of a rubber stopper a short bulb tube about 12 mm. in diameter, terminating in a longer tube which has a bore of slightly over 4 mm. The bulb of this tube (deposition tube) is loosely filled with clean absorbent cotton which has been kept over sulphuric acid to insure uniform dryness. Instead of the bulb tube, the rubber stopper of the exit tube may carry a short piece of glass tubing of about 12 mm. diameter, in which is placed the absorbent cotton, and to which, by means of another rubber stopper, is attached the deposition tube.

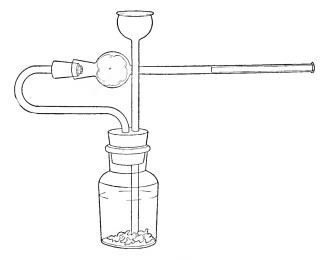


FIGURE A.

The simplicity and compactness of this apparatus allow a number of determinations to be carried on at the same time by the use of several pieces. It is important, however, that the bottles be of the same size, and it is also advisable to have the rest of the apparatus of as nearly definite size as possible.

Reagents. We have used zinc and hydrochloric acid in preference to zinc and sulphuric acid, as the action goes on more regularly and without the addition of a sensitizer. The chance for the formation of hydrogen sulphide is also less. The zinc, known as Bertha spelter, is from the New Jersey Zinc Company of New York, and has been proved by exhaustive tests to be free from arsenic. It contains not over 0.019

per cent of lead and not more than 0.013 per cent of iron. The hydrochloric acid is obtained of the Baker and Adamson Company of Easton, Pennsylvania, and has been shown by careful analysis to contain not over 0.02 milligram of arsenious oxide per liter. The dilution employed, one part of acid to six of water, is equivalent to a normality of about 1.5. The quantity of diluted acid used in the analysis would not contain over 0.00004 mg. of arsenious oxide, an amount beyond the practical limit of the delicacy of the method. No evidence of sulphur, phosphorus, antimony, or arsenic has been obtained from these reagents when used in long continued blank tests.

Procedure. Three grams of carefully and uniformly granulated zine are placed in the bottle, and a strip of sensitized paper is slipped into the deposition tube to a definite distance, the paper being wholly within the tube. Fifteen cubic centimeters of diluted acid are then added through the thistle tube, and the evolution of hydrogen is allowed to continue for at least ten minutes. At the end of this time the rate of flow of the gas has become as regular as possible, and the atmosphere in the deposition tube has a nearly definite degree of saturation with aqueous vapor. On these two conditions depends chiefly the uniformity of color bands from equal amounts of arsenic. In this time, also, the absence of arsenic in reagents and apparatus is assured, in the great majority of cases, by the non-appearance of color on the sensitized paper, but the blank test may be as long continued as circumstances demand.

The solution to be tested is then introduced, either wholly or in aliquot part, which may be determined by weighing or measuring. In the former case we use a side-neck test tube of about 30 c.c. capacity, and weigh to the second decimal place. Unless the amount of arsenic be exceedingly small, it is not necessary to add the whole of the solution, but in that case the volume must be obviously not over 15 c.c., on account of the capacity of the bottle.

After introduction of the solution the color appears upon the paper in a few minutes and the deposit reaches its maximum within thirty minutes. The band of color thus obtained is then compared with a set of standard bands. From the amount of arsenic as estimated from the comparison, and the amount of solution from which the band was obtained, the calculation of the arsenic in the entire solution is simple.

<sup>8</sup> We are also indebted to the Baker and Adamson Company for a preparation of hydrochloric acid containing a still smaller quantity of arsenic, the use of which will be later explained in the discussion of the absolute delicacy of the method.

Standard Color Bands. A standard solution is made by dissolving one gram of re-sublimed arsenious oxide in a small quantity of sodic hydroxide free from arsenic, acidifying with sulphuric acid and making up to one liter with recently boiled water. Of this solution (I) 10 c.c. are diluted to a liter with freshly boiled water, giving a solution (II) which contains 0.01 mg. or 10 micromilligrams (mmg.) of arsenious oxide per cubic centimeter. In testing the delicacy of the method we have also prepared solutions containing 1 mmg. (III) and 0.1 mmg. (IV) per cubic centimeter.

From definite portions of solution II, measured from a burette, a series of color bands is made by the above procedure, using a fresh charge of zinc and acid for each portion. Figure 1 (Plate 1) shows in colors the actual size of the set of bands made by us, corresponding to the following amounts of arsenious oxide in micromilligrams: 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70. The color in the lowest values is a lemon yellow, shading from this to an orange yellow and through orange yellow to reddish brown in the higher values.

Preservation and Development of the Color Bands. The rapid fading of the stains has been a serious obstacle to the use of the Gutzeit reaction for a quantitative method, and it became very soon evident to us that some means of preserving the color bands must be found before the method could be considered an entirely practical one. It was clear that the chief factors in the change of color were light and moisture, the latter being by far the more important. Concerning the mechanism of the reactions, either for the formation of the color or for its decomposition with water, the work of those who have investigated the reactions was not sufficient to guide us.

The early work of Rose <sup>9</sup> on the action of arsine on excess of mercuric chloride in solution showed that a yellowish brown precipitate was formed having the empirical formula AsHg<sub>3</sub>Cl<sub>3</sub>. This was considered by Rose to be made up of mercurous chloride and a compound of mercury and arsenic, to which the formula As<sub>2</sub>Hg<sub>3</sub> might be given.

Mayençon and Bergeret <sup>10</sup> consider the compound to be a mixture of arsenic and mercurous chloride.

Franceschi, <sup>11</sup> apparently without knowledge of Rose's work, passed arsine through an aqueous solution of mercuric chloride. The liquid became at first a light yellow, then red, and there was precipitated a substance at first yellow, but with excess of gas a dark red, "of the

<sup>&</sup>lt;sup>9</sup> Pogg. Annal., **51**, 423 (1840).

<sup>10</sup> Comptes Rendues, **79**, 118 (1874).

<sup>&</sup>lt;sup>11</sup> L'Orosi, **13**, 289 (1890).

color of Spanish tobacco." For this compound Franceschi assumes from the analysis and properties the formula AsHHg<sub>2</sub>Cl<sub>2</sub>, which he writes:

$$\begin{array}{c} - \ \mathrm{H} \\ - \ \mathrm{HgCl} \\ - \ \mathrm{HgCl} \end{array}$$

Lohmann,<sup>12</sup> who does not mention the results of Franceschi, finds the reaction to run in a similar manner. But the red product decomposed with water, becoming black, and with such rapidity that an analysis was impossible except through the decomposition products. From this the formula AsHg<sub>3</sub>Cl<sub>3</sub> was assigned. Lohmann considers that the reaction is always

$$3 \operatorname{HgCl}_2 + \operatorname{AsH}_3 = \operatorname{AsHg}_3 \operatorname{Cl}_3 + 3 \operatorname{HCl}$$
,

whether the precipitation is complete or not, and that the decomposition of the product depends (a) on the presence of mercuric chloride, in which case arsenic and mercurous chloride are the products, or (b) on absence of mercuric chloride, in which case mercury, arsenious acid, and hydrochloric acid are the products.

Partheil and Amort <sup>13</sup> note the formula given by Franceschi, AsHHg<sub>2</sub>Cl<sub>2</sub>, but evidently assume that it was for the yellow body (if such indeed exists) and not for the red, which was clearly indicated from Franceschi's paper. On this assumption and from Lohmann's work, they consider that the following is the reaction for the formation of the yellow body:

$$2 \; \mathrm{HgCl_2} + \mathrm{AsH_3} = \mathrm{AsHHg_2Cl_2} + 2 \; \mathrm{HCl}$$

and for the red:

$$3 \operatorname{HgCl}_2 + \operatorname{AsH}_3 = \operatorname{AsHg}_3\operatorname{Cl}_3 + 3 \operatorname{HCl}$$

These reactions were given by Franceschi and by Lohmann respectively, but both of these authors were dealing with the red body. Partheil and Amort further consider these bodies to have the following structure, respectively:

$$\begin{array}{ccc} -H & -H gCl \\ As - HgCl & and & As - HgCl \\ -HgCl & -HgCl \end{array}$$

<sup>12</sup> Pharm. Zeitung, **36**, 748 and 756 (1891)

<sup>13</sup> Ber. d. deutsch. Chem. Gesell., 31, 594 (1898).

Passing excess of arsine through the solution in which the red body is suspended, Partheil and Amort obtain a black precipitate to which they give the formula As<sub>2</sub>Hg<sub>3</sub>, and this derives support from the reactions with alkyl iodides described by these authors in a succeeding paper. 14 The investigation is given somewhat more fully in a later paper by Partheil. 15 On partial precipitation of a mercuric chloride solution by arsine, a yellow body was obtained, to which, from a single analysis of an evidently impure substance, the formula AsH<sub>2</sub>HgCl was assigned. From this experiment and from the results of Franceschi and of Lohmann, Partheil considers that there should be added to the two substances given above a third, with the structure

$$\begin{array}{l} - \ H \\ - \ H \\ - \ H_g C l \end{array}$$

While the evidence appears to show that the hydrogen of arsine is replaced by the mercurous chloride group to a greater or less extent, the formula for the red substance does not seem to us to have been conclusively proved, and the reactions of decomposition are decidedly Nothing has been brought forward to show definitely the relation of the vellow compound or compounds, if such exist, to the red. Lack of time prevents us at present from studying the reaction quantitatively, but it is hoped that the investigation may be taken up later by one of us. Nevertheless the following qualitative reactions have made it possible to treat the bands of color so that they may be kept for a considerable time, either in their original form or by means of a quasi development and fixation.

The removal of the relatively large excess of mercuric chloride from the paper by treatment with absolute ether or alcohol did not offer a solution of the difficulty, as the colors faded rapidly even when kept in the dark and over sulphuric acid. The color is quickly bleached by boiling with water, as is well known. Cold water acts more slowly, the color not being completely changed until after a day or two, and then not bleached, but converted to a dull gray. Bird, 16 and also Goode and Perkin, <sup>17</sup> have observed the action of hydrochloric acid upon the original color, which is thereby considerably changed. Goode and Perkin also note the action of ammonia upon the original color, but do not find the action of service in preparing standards.

From the evident effect of even a slight amount of moisture we were

<sup>&</sup>lt;sup>14</sup> Ibid., **31**, 595 (1898).

Archiv. d. Pharm., 237, 121 (1899).

<sup>16</sup> Loc. cit.

<sup>17</sup> Loc. cit.

led to adopt the suggestion of Panzer, <sup>18</sup> as applied to the standard Marsh mirrors, for the preservation of our standards. A clean, dry, glass tube, about 5 mm. in diameter, is scaled at one end, at which is placed a small quantity of phosphorus pentoxide covered by a bit of dry cotton wool. The strip is then inserted, colored end down, fastened by a drop of Canada balsam, and the tube is scaled. The set of standards prepared in this way can be used for several months, although the brilliancy of the color is lost after a few weeks.

The color band may be developed by treatment with rather concentrated hydrochloric acid, of a normality of about 6 (one part acid to one of water). This is done in a small test tube, at a temperature not exceeding 60° and for not over two minutes, else, with this concentration of acid, the paper is likely to become disintegrated. The strip is then thoroughly washed with running water and dried. The color on the wet strip is a brilliant dark red in the higher values, while the smaller amounts show a deeper yellow than in the initial set. The length of the bands is considerably greater than that of the original. On drying, the color becomes duller. These bands must also be sealed as above with phosphorus pentoxide, and are somewhat more permanent than the initial set. Figure 2 (Plate 1) represents the set obtained by development of the initial set with hydrochloric acid.

If the original color band is treated for a few minutes with normal ammonic hydroxide, a dense coal black color is produced, of slightly greater length than the original. This color is far more permanent than the others, but it is nevertheless necessary to seal the dry strips in glass, using fresh, powdered quicklime instead of phosphorus pentoxide. Figure 3 (Plate 2) shows the set obtained by development of the initial set with ammonia.

#### General Precautions.

As far as concerns the reduction of the arsenic, no other precautions are necessary than those which must be observed in the proper conduct of the Berzelius-Marsh method when applied to small amounts. The solution to be reduced should contain no interfering organic matter, nor any metals which prevent or retard the formation of arsine. Sulphur in any form reducible to hydrogen sulphide should be absent. It is well known that small amounts of hydrogen sulphide interfere with the Gutzeit reactions, and it is the custom of most analysts to pass the arsenical hydrogen over paper or cotton wool containing plumbous acetate, or even through a lead solution, before it reaches the mercuric

<sup>18</sup> Zentralbl., 74 (1), 821 (1903).

chloride. As we have been careful to eliminate the sulphur before testing, we have not found this necessary, except in certain cases, when, with a sufficiently long deposition tube, it is very simple to insert a strip of paper saturated with normal plumbous acetate and dried. Phosphites and hypophosphites will also have been oxidized before introduction of the solution, and there is little danger in ordinary work from small amounts of phosphine which might result from the accidental presence of reducible compounds of phosphorus. Antimony should of course be absent, but very small amounts of stibine do not interfere with the recognition, though they may prevent the estimation of arsenic. Free nitric acid must be avoided. Arseniates require especial treatment, as will be discussed below.

#### Special Precautions.

In order to be certain of uniformity in length and color of the bands from the same amount of solution, the following points must be observed:

- 1. The reduction bottles must be of equal capacity and the deposition tubes of equal bore.
- 2. The amount of zinc must be the same always, and the granulation must be uniform.
  - 3. The volume and concentration of the acid must be definite.
- 4. The absorbent cotton must be perfectly clean and reasonably dry, and is therefore best stored in a desiccator before use. The amount used should be approximately the same in all cases, packed in the bulb tube to about the same density.
- 5. The sensitized paper must be acted upon by a gas in which the moisture is as nearly constant as possible. For this reason the paper cannot be allowed to become moist, nor can the gas be dried. In the first case the band is short and imperfectly shaded; in the second, it is scattered along the whole length of the strip, or even partially escapes the paper. This we have shown by attaching a hard glass tube with capillary, in which, on heating, a mirror of arsenic was obtained. Conversely, under carefully regulated conditions, no evidence of escaping arsenic was found, either by the use of a hot tube or by the introduction of a second strip of sensitized paper.
- 6. After ten or twelve runs with the same bottle, the atmosphere of the deposition tube becomes too moist, and the bands are consequently too short. It is then necessary to replace the cotton. In order to get a sufficient degree of saturation in the next run, the evolution of hydrogen must go on for a longer time than usual before adding the

test solution, say for an hour. This preliminary saturation may be also conveniently secured by leaving zine and acid in the apparatus over night.

By observation of the above precautions we have obtained fairly regular and uniform bands of color from equal amounts of arsenic, —

TABLE I.

|                     |                                                                   |                                         |                                                                 | W                |                                    |                                                   |                           |
|---------------------|-------------------------------------------------------------------|-----------------------------------------|-----------------------------------------------------------------|------------------|------------------------------------|---------------------------------------------------|---------------------------|
| No. of<br>Analysis. | $egin{aligned} \mathbf{As_2O_3} \\ \mathbf{taken.} \end{aligned}$ | Total<br>Weight<br>Diluted<br>Solution. | Weight<br>Diluted<br>Solution<br>taken for<br><b>A</b> nalysis. | Reading of Band. | $\mathbf{A}s_2\mathbf{O}_3$ found. | As <sub>2</sub> O <sub>3</sub><br>found,<br>Mean. | Per cent $As_2O_2$ found. |
|                     | mg.                                                               | grm.                                    | grm.                                                            | mg.              | mg.                                | mg.                                               |                           |
| 6                   | 0.05                                                              | 21.21                                   | 5 7 5                                                           | 0.009            | 0.033                              | 8.                                                |                           |
| Ů                   | *****                                                             |                                         | 6.05                                                            | 0.012            | 0.043                              | 0.038                                             | 76                        |
| 8                   | 0.10                                                              | 24.13                                   | 5.74                                                            | 0.024            | 0.100                              |                                                   |                           |
| Ü                   | 0.10                                                              | 21.10                                   | 7.16                                                            | 0.027            | 0.091                              | 0.096                                             | 96-                       |
| 2                   | 0.25                                                              | 24.95                                   | 3.5                                                             | 0.037            | 0.26                               |                                                   |                           |
| -                   | 0.29                                                              | 24.00                                   | 2.7                                                             | 0 025            | 0.23                               | 0.25                                              | 100                       |
| 1                   | 0.50                                                              | 26.11                                   | 1.0                                                             | 0.018            | 0.47                               |                                                   |                           |
| 1                   | 0.50                                                              | 20.11                                   | $\frac{1.0}{1.3}$                                               | 0.018            | 0.50                               | 0.49                                              | 98                        |
| _                   |                                                                   | 25.03                                   | 0.00                                                            | 0.014            | 2.50                               |                                                   | 1                         |
| 7                   | 1.00                                                              | 25.02                                   | 0.39<br>0.76                                                    | $0.014 \\ 0.028$ | $0.90 \\ 0.92$                     | 0.91                                              | 91                        |
|                     |                                                                   |                                         |                                                                 |                  |                                    | 0.51                                              | 31                        |
| 9                   | 1.00                                                              | 23.76                                   | 0.35                                                            | 0.013            | 0.88                               | 0.00                                              | 00                        |
|                     |                                                                   |                                         | 0.48                                                            | 0.022            | 1.09                               | 0.99                                              | 99                        |
| 3                   | 1.50                                                              | 23.88                                   | 0.47                                                            | 0.027            | 1.37                               |                                                   |                           |
| •                   |                                                                   |                                         | 0.47                                                            | 0.027            | 1.37                               | 1.37                                              | 92                        |
| 4                   | 2.00                                                              | 25.51                                   | 0.66                                                            | 0.055            | 2.15                               |                                                   |                           |
|                     |                                                                   |                                         | 0.51                                                            | 0.035            | 1.75                               | 1.95                                              | 98                        |
| 5                   | 2.50                                                              | 27.04                                   | 0.19                                                            | 0.015            | 2.13                               |                                                   |                           |
|                     | 2.30                                                              |                                         | 0.34                                                            | 0.028            | 2.24                               | 2.19                                              | 88                        |
|                     |                                                                   |                                         |                                                                 |                  |                                    |                                                   |                           |
| A                   | Average pe                                                        | rcentage .                              |                                                                 |                  |                                    |                                                   | . 93                      |
|                     | z.c.age pe                                                        |                                         |                                                                 |                  |                                    |                                                   | . 50                      |

using apparatus of definite size, reagents of definite concentration, carefully sensitized paper, and by passing the arsenical gas over the paper in a condition of moisture which is as carefully regulated as possible. Without these precautions, which involve no great care, the method will not give satisfactory quantitative results.

#### ANALYTICAL DATA.

The method, as far as it concerns the determination of arsenic in a solution properly prepared for reduction, was tested by the analyses of solutions containing varying amounts of arsenic, which, with the exception of Nos. 5, 8, 7, and 9, were unknown to the analyst (see Table I). In analysis No. 9 the arsenic was present as arsenic acid. In Nos. 5, 8, 7, and 9, the comparison was made with standards which had been kept over three months, and the reading of the bands was confirmed by the standards obtained by development of the initial bands with ammonia.

We do not claim for the method, under ordinary circumstances, a greater accuracy than from five to ten per cent.

# ANALYTICAL NOTES.

Sensitized Paper. We have found that the prepared paper, if kept dry and away from the light, does not lose its sensitiveness to a great extent after several months. On long keeping there is apparently a very slight reduction to mercurous chloride, since an old paper after treatment with hydrochloric acid and washing gives a slight darkening with ammonia or auric chloride (for this test, see below). Although this change does not greatly influence the result, it is better not to use paper which has been kept too long.

Contrary to Goode and Perkin, <sup>19</sup> we have found no advantage in using mercuric bromide instead of the chloride. Neither the aqueous solution of the former, which is, in addition, too dilute, nor the alcoholic solution, gives a paper of greater sensitiveness than that prepared from the chloride. The alcoholic solution of the chloride, since it evaporates more rapidly, leaves a less even surface of the salt upon the paper than is obtained by the slower evaporation of the aqueous solution.

Apparatus. In case it is necessary to examine larger quantities of solution for arsenic, a larger reduction bottle will naturally suggest itself. In this case, slight variations from the procedure may be found necessary, and the absolute delicacy of the method may be somewhat less.

We have found no sign of arsenical contamination from the rubber stoppers used in the apparatus, and we have therefore not lessened the simplicity of the apparatus by making it entirely of glass. The stoppers are boiled with dilute alkali and washed before use.

Although we have not tried it for ourselves, it would seem obvious that the electrolytic reduction of the solution could be employed if desired.

Reagents. From the delicacy of the method, as discussed below, the zinc used by us is evidently highly sensitive. Indeed, the amount of iron present, to which metal, from the work of Chapman and Law, 20 Parsons and Stewart, 21 and others, may be attributed the insensitiveness of most samples of zinc, is about one-seventh of the amount in a zinc which Chapman and Law show to be sufficiently sensitive in the Marsh process.

We have also in this connection studied the effect of the presence of other metals on the sensitiveness of the zinc. The retention of arsenic by the addition of platinic chloride or cupric sulphate, confirmed by one of us 22 (S) several years ago, is well known. With a bright platinum foil in contact with our zine and using either sulphuric or hydrochloric acid, we have never noticed any loss of arsenic in the Marsh procedure. Similarly, there is no diminution in the delicacy of our method when platinum foil is used. The use of zinc carefully covered with copper after the procedure of Lockemann 23 makes no difference whatever in the results, nor does the addition of tin or lead salts to the solution during the reduction.

The zinc is granulated by pouring the metal, melted in a porcelain casserole, from a height of six feet through a hot porcelain sieve into two feet of cold water.

The estimation of the arsenic in the hydrochloric acid was made on samples of 100 c.c. in two ways. The acid was distilled to half its volume, a treatment which we have shown in the following paper 24 to be sufficient to expel all the arsenic. The distillate was collected in 35 c.c. nitric acid and evaporated with a small amount of sulphuric acid. Again, the acid was allowed to drop slowly into hot nitric acid and the mixture was then evaporated. Several residues obtained by both of these procedures from lots of 100 c.c. gave closely agreeing results, both from the reading of the Marsh mirrors and the Gutzeit color bands. The mean of all determinations was 0.002 mg. for 100 c.c., or 0.02 mg. per liter.

<sup>20</sup> Analyst, 31, 3 (1906).

<sup>21</sup> Jour. Amer. Chem. Soc., 24, 1005 (1902).

<sup>&</sup>lt;sup>22</sup> These Proceedings, 26, 24 (1891); Amer. Chem. Jour., 13, 431 (1891).

<sup>23</sup> Zeitschr. f. angew. Chem., 18, 416 (1905).

<sup>24</sup> These Proceedings, 43, 327 (1907); Jour. Soc. Chem. Ind., Vol. 26 (1907); Zeitschr. f. anorg. Chem., Vol. 56 (1907).

This acid was shipped in carboy, and we have not observed any increase of arsenic in the acid on standing, such as might result from the action upon the glass if the latter contained arsenic. It is better, however, that such acid should be shipped, or at least stored, whether concentrated or dilute, in ceresine bottles.

We have noticed that the nitric acid from the carboy, which gave no test for arsenic, took up traces from the storage bottle on long standing. We have therefore stored the nitric acid in ceresine. A slight but unimportant amount of paraffine is taken up. 50 c.c. lots of this acid, evaporated with a small quantity of sulphuric acid, gave residues which showed no traces of arsenic. It must be borne in mind that a nitric acid residue contains the arsenic as arsenic acid and that the procedure must accordingly be modified as explained below.

The second sample of hydrochloric acid, referred to in the footnote above, was shipped in ceresine, and the diluted acid is also kept in ceresine. Two 100 c.c. lots of this acid were dropped into nitric acid and evaporated with sulphuric acid. The residues were reduced with sulphurous acid free from arsenic and gave color bands equal to 0.3 and 0.5 mmg. arsenious oxide respectively. This is equivalent to 0.004 mg. of arsenious oxide per liter.

Procedure. At the end of a run, a slight annular sublimate is often observed on the inside of the deposition tube where the color band is in contact with the glass. With very small amounts of arsenic this sublimate is white, but is ordinarily slightly colored. It is probably due to transference of mercuric chloride, either through volatilization or capillary action, and a slight color reaction may take place on the deposit. The amount is without influence on the result, but the tube should be cleaned with a bit of dry cotton before being used again.

The temperature during reduction should not be allowed to rise very much, as the moisture equilibrium in the deposition tube is disturbed from the excess of moisture carried over. For this reason the procedure of Bird, 25 which consists in heating the liquid under reduction to the boiling point, is not adapted to this method.

We have found no advantage in using very large amounts of zine, as recommended by many, especially in the Marsh process, nor do we think it necessary that the zine should be entirely dissolved.

Standard Bands. We have long noticed that solutions of the dilution of 0.01 mg. per cubic centimeter undergo a change on standing,

with the result that a given volume will not yield the same depth of band as when first prepared, or, in the Marsh process, the same intensity of mirror. In more dilute solutions the change is very rapid, and solution IV, containing 0.1 mmg. per cubic centimeter, is of no value as a standard in a day or two. The use of boiled water for dilution greatly retards the change, which would lead to the conjecture that the reaction might be one of oxidation, with formation of arsenic acid, which, as shown below, does not give the same depth of color in a given time as its equivalent of arsenious acid. Yet the treatment of an old solution with sulphurous acid does not increase the amount of arsenic from a given portion of it, as far as we have been able to determine. Solution IV (0.1 mmg.) should be freshly prepared before use; solution II (10 mmg.) will hold its strength for a few weeks, and solution I (1 mg.) should not be used if it has stood for a very long time.

The deposit of color is of course on both sides of the paper. If the strip exactly bisects the tube and the flow of hydrogen is the same in both segments, the intensity of color should be the same on each side of the strip. It often happens that there is a slight difference, and in consequence the band may appear on one side greater than the standard, on the other less. The set of standards is also a series of mean, though not greatly varying color densities, and when viewed from one side or the other may not seem regularly graded. The set should be mounted in such a way that both sides of the strip can be examined, and the mean density of the test band should be compared with the mean density of the standard. The judgment is greatly assisted by treating the band or its duplicate with hydrochloric acid or ammonic hydroxide (particularly the latter), and comparing the result with the corresponding standards.

Treatment of the Bands. Whatever may be the formula of the red compound, it is probable that the reaction is only complete in the presence of an excess of hydrochloric acid. As previously mentioned, the color fades completely on treatment with hot water. Cold water brings about a gradual fading, but this is succeeded by a secondary reaction by which a gray substance is formed. This action of water was further studied by treatment with sodic acetate. A set of standard bands was immersed in half-normal sodic acetate for two hours in the cold. The red color gave place to a uniformly graded light yellow with a tinge of orange. The set, after pressing between filter paper, was then sealed while still moist. In twenty-four hours the yellow had changed to a dull white, with no color except in the higher values.

On the next day there was a change to a faint gray, becoming darker on further standing.

The black color with ammonic hydroxide suggests the presence of mercurous chloride, but it is not clear whether a decomposition into mercurous chloride takes place before the black color is formed. If the red band is treated with hydrochloric acid, washed, and then placed in ammonic hydroxide, the color is not an intense black, but rather grayish in tone.

Another reaction of interest is that with auric chloride. If the band, after treatment with hydrochloric acid, is placed in a small test tube with a few drops of hundredth normal auric chloride and allowed to stand for five or ten minutes, a beautiful purple color results. The reaction is characteristic for larger amounts of arsenic.

The reaction of the formation, development, and decomposition of the color bands are susceptible of various interpretations, but, as we have said before, a quantitative study is necessary before expressing an opinion, not only as to the formula of the red body and the mechanism of its formation and decomposition, but also on the existence of intermediate yellow compounds or their formulae.

Bird <sup>26</sup> has applied Bettendorff's reaction to the stains, substantially as follows: The disk of paper containing the color is extracted with one or two cubic centimeters of warm, concentrated hydrochloric acid. The extract is oxidized by a few drops of bromine in hydrochloric acid and treated in a small test tube with an equal volume of 30 per cent stannous chloride. On warming, the pinkish brown color appears.

# Interference of the Hydrides of Sulphur, Phosphorus, and Antimony.

There is considerable confusion in the statements of various authors as to the color stains from these gases on mercuric chloride paper, and even Bird's more careful study is open to the common criticism that the descriptions are not given with reference to known amounts of the hydrides. In determining to what extent these substances interfere in our method, we have at first ascertained by trial how much of the particular hydride will give a comparable band on the mercuric chloride paper under the same conditions, — particularly in the same time. We then studied the effect of a given treatment upon each color band, and afterward compared the effect of each reagent upon the four approximately equivalent bands.

Hydrogen Sulphide. In a freshly prepared solution of sulphurous acid, which gave no test for arsenic, the amount of sulphur was determined by titration with iodine. A solution was made containing 1 mg. of sulphur per cubic centimeter, and from this, in turn, a second containing 0.01 mg. Of this solution amounts corresponding to 10, 30, 50, and 70 mmg. sulphur were added to separate reduction bottles and the action continued for thirty minutes. Bands of a pale yellow were obtained, slightly darker in shade than those from phosphine. The respective lengths corresponded to those from 2, 25, 30, and 40 mmg. arsenious oxide. Fresh strips of paper were now substituted and each experiment was continued for thirty minutes longer. No additional band was obtained from the first; from the others the values were approximately 1, 5, and 10 mmg. This shows that under the same conditions and in equal time the band from 50 mmg. sulphur will be of about the same length as that from 30 mmg. of arsenious oxide, and further, that the reduction of the sulphurous acid is not completed in thirty minutes, like the arsenic, but requires a longer time.

The color of the sulphur band is somewhat brightened by hydrochloric acid (6 N) but not essentially changed, nor was the length increased. Auric chloride produced a dirty light brown. Ammonia

on the original band gave also a light brown color.

Phosphine. A sample of sodic hypophosphite, containing no arsenic on testing, was shown by analysis to contain 28.94 per cent of oxidizable phosphorus (theory, 29.23). Of this a solution was made containing 1 mg. of phosphorus per cubic centimeter, from which two others were prepared having 0.1 and 0.01 mg, to the cubic centimeter. Of the last solution, 10, 30, 50, and 70 mmg. were reduced for thirty minutes in separate bottles. From 10 mmg. no color was obtained, from 30 mmg. a very faint indication, and from 50 and 70 mmg. bands corresponding in length to only about 2 and 10 mmg. of arsenious oxide respectively. After continuing the action for thirty minutes longer, with fresh strips, there was again no color on the first, a faint indication on the second, and about 1 and 10 mmg, on the third and fourth. was evident that the reduction was very slow. Next were taken 100, 300, and 500 mmg. After thirty minutes the length of the first band corresponded to about 2 mmg, of arsenious oxide, the second 30, and the third 50, showing that not over one tenth of the phosphorus had been reduced in the given time. On opening the bottles the odor of phosphine was strong.

To obtain a band from the hypophosphite equal to that from 30 mmg. arsenious oxide in the standard time, an amount equivalent to 200 or 300 mmg. phosphorus is necessary. The color of the bands was a bright yellow, somewhat resembling that from hydrogen sulphide. Hydrochloric acid makes the band a bright lemon yellow, but without increasing its length. The yellow turns slowly brown when exposed to light. Auric chloride acts very slowly, giving at first a characteristic brownish red, which changes to purple. Ammonia acts more slowly than on the arsenic band, giving a less intense black.

The solutions used were made from a sample of pure tartar emetic, which had been shown to be free from arsenic. They contained respectively 1.0, 0.1, and 0.01 mg. of antimonious oxide per cubic centimeter. Volumes corresponding to 10, 30, 50, and 70 mmg. of the oxide were added to separate bottles and the reduction carried on for thirty minutes. No color was obtained in any case. Hydrochloric acid did not develope. Auric chloride brought out slowly a purple color, duller finally than that of a similarly treated arsenic band. Ammonia turned the band quite quickly black, and a comparison with the arsenic ammonia standards showed amounts equal to about 20 to 40 per cent of the arsenic values. On further reduction for thirty minutes, with fresh strips, there was no additional deposit on the paper which could be developed by ammonia. Continuing the experiments, it was found necessary to add 100 mmg. of antimonious oxide before any visible band was obtained, and 200 mmg. before the band appeared to be of the same length as that from 30 mmg. of arsenious oxide. The color was a faint gray when first visible; darker with increasing amounts. The development with hydrochloric acid and auric chloride or with ammonia showed of course that the paper had been originally affected over a much greater length than was then visible.

These results agree with those obtained by Franceschi,<sup>27</sup> who found by the action of stibine on mercuric chloride a white body to which he gave the formula SbHHg<sub>2</sub>Cl<sub>2</sub>, analogous to the formula assigned by him to the red arsenic compound. Dowzard,<sup>23</sup> also, was unable to obtain a stain on mercuric chloride paper from 0.01 to 0.1 mg. of tartar emetic, while from 0.2 mg. he got a faint blackish brown color, a result which is essentially confirmed by our experiments.

Comparative Effect of Reagents. From the necessary amounts of each substance, as shown by the above trials, approximately equal color bands were prepared from arsine, stibine, phosphine, and hydro-

<sup>&</sup>lt;sup>27</sup> L'Orosi, **13**, 397 (1890).

<sup>28</sup> Jour. Chem. Soc., 79, 715 (1901).

gen sulphide, with a reduction of thirty minutes' duration. Each set of four was then treated with various reagents and the effects compared.

Initial Band. The arsenic band appears in a few minutes and is nearly complete before the others begin to form. The deposit is characteristic and unmistakable. The phosphorus and sulphur bands are a uniform pale yellow, rather difficult to distinguish from each other. The antimony band is a faint gray.

Exposure to Air. On standing over night in rather moist, warm air, the arsenic band was slightly bleached, the others unchanged. On longer exposure the phosphorus band was turned slightly brown on the upper side, and the sulphur band became slightly dark on the upper edge. Heating to 105° had no additional effect on any of the bands.

Cold Water. The initial set was placed in cold water. After fifteen minutes the antimony band was bleached completely, the phosphorus became paler, while the arsenic and sulphur were unchanged. After fourteen hours the arsenic was considerably bleached, but was still orange red, while the phosphorus had become a very faint yellow and the sulphur was unchanged.

Hot Water. The set was boiled with water for one minute. The arsenic and antimony bands were changed to a grayish white, the phosphorus was bleached to a faint yellow, while the sulphur was unchanged. On standing, the sulphur band became light brown.

Hydrochloric Acid. The set was warmed to 60° with hydrochloric acid (6 N) for one minute and thoroughly washed. The arsenic band was lengthened and became the usual brilliant red. The antimony was turned slightly gray. The phosphorus became a brilliant lemon yellow, and the sulphur was also brightened, but not so strikingly. On drying, the colors became duller, and on the upper end of the sulphur band was a fringe of dark gray.

Auric Chloride. The dried set from the last treatment was immersed in auric chloride (n/100) for five minutes. The arsenic band became at once a brilliant purple; the antimony changed more slewly. The phosphorus slowly turned a characteristic red brown, then to purple, and the final colors of these three bands differed chiefly in intensity. The sulphur band had only a slight brownish tinge.

Amnronia. The set was placed in normal ammonic hydroxide for five minutes. The arsenic band became at once a brilliant black; the antimony also quickly, but the band was longer and duller in shade. The phosphorus turned slowly black and was not equal finally to the other two in intensity. The sulphur band was not blackened, but changed slightly to a pale brown, somewhat darker on drying.

From these results it will be seen that if we have a color band from pure material, within or above the range of the 4 mm. arsenic standards, the differentiation of arsenic from antimony, phosphorus, and sulphur is perfectly simple. With smaller amounts, or especially with mere traces, there can be no confusion with antimony, since stibine gives no yellow color on the paper. With sulphur, while the small initial band might be mistaken for arsenic, the treatment with hot water, ammonia, and auric chloride will easily identify it. But with phosphorus there is likely to be a doubt if the 2 mm. band 29 is very small, since the amount and length of the color do not permit the same comparison as in the larger bands. As we have shown, however, that even as much as 0.1 mg. of phosphorus gives very little color in thirty minutes of reduction, and as this is a quantity which can be easily oxidized in the preparation of the solution for analysis, we should have little to fear from smaller amounts than 0.1 mg. Such amounts might be considered quite accidental.

Effect of Hydrogen Sulphide, Phosphine, or Stibine on the Arsenic Band. Very different is it, however, when the arsenic solution also gives by reduction as much of any one of these gases as would alone yield a band equal to the arsenic band in length. This is shown by the following experiments.

Hydrogen Sulphide. Amounts of the respective solutions, equal to 30 mmg. of arsenious oxide and 50 mmg. of sulphur, were added together to a bottle and reduced for thirty minutes. Instead of the short, well-defined band of the arsenic, a band nearly three quarters of the length of the strip was formed, of a reddish yellow color. Hydrochloric acid turned it slightly redder, but the appearance was not definitely characteristic of arsenic. On another similar band ammonia brought out splotches of black on a red ground. The arsenic had evidently acted as an accelerator in the reduction of the sulphurous acid, and the resulting band was due to a mixture of the arsenic and sulphur compounds, spread over a greater surface.

Phosphine. Solutions containing 30 mmg. arsenious oxide and 200 mmg. phosphorus were added to a bottle and reduced for thirty minutes. The band was longer than the corresponding band of arsenic, but with the characteristic appearance of the latter, — well shaded, except that it was somewhat lighter at the top. Hydrochloric acid converted the color to the well-marked red of arsenic and the length agreed with the hydrochloric acid standard for 30 mmg. Auric

<sup>29</sup> For the use of the 2 mm. band, see below.

chloride acted more slowly than with arsenic alone, giving a slight brownish red at first and finally a somewhat lighter purple than the pure arsenic color. There was apparently little increase in evolution of phosphine in the presence of the arsenic, and the arsenic compound in the mixed band was not appreciably obscured.

Stibine. Solutions containing 30 mmg, arsenious oxide and 70 mmg, antimonious oxide were reduced together for thirty minutes. The resulting band was pale red in color and over twice as long as the band from 30 mmg, of arsenious oxide. Hydrochloric acid gave a color not essentially different, which faded on drying to a rather dirty brownish red. The evolution of the two hydrides was apparently more rapid than either alone, and the mixed band was longer than from either amount.

It is evident from the above results that if we have with the arsenic an amount of hydrogen sulphide even below that required to give a band of the same length as the arsenic, the latter will be so altered as to make its quantitative estimation impossible and its detection doubtful. But, as unavoidable amounts of hydrogen sulphide would be held back completely by lead acetate paper, we should have no difficulty in estimating the arsenic if the solution had not been properly oxidized before testing. Even if the solution contains considerable reducible sulphur, the lead acetate paper will protect the mercuric chloride strip.

We have also little to fear from phosphine, since we should not put a solution into the reduction bottle until the phosphorus had been oxidized as completely as possible. Accidental amounts of phosphine would not affect the quantitative estimation of the arsenic. We have not thought it necessary, for this reason, to verify the statement of Dowzard 30 that phosphine is held back by cuprous chloride in hydrochloric acid solution, nor have we sought any other reagent which could be adapted to this purpose under the conditions of our method.

In the presence of stibine arsenic may be qualitatively recognized, but not quantitatively determined, when the amount of antimony is enough to give, if alone, an ammonia band equal to that of the arsenic. But we should not test a solution without getting rid of any antimony it might contain, and the methods for that purpose are satisfactory. Slight traces of antimony would not affect the determination.

If the arsenic is accompanied by any two or all three of the substances in question, cases which we think would seldom arise, their influence on the determination of the arsenic could be predicated from the foregoing investigation.

To sum up, then, we think that small amounts of arsenic can be determined by our method without danger of interference from sulphur, phosphorus, and antimony, provided the solution to be tested is freed as carefully as possible from these substances and the additional precaution is taken to place a strip of lead acetate paper in front of the test paper.

From the comparative rarity of the hydrides of selenium and tellurium and the unlikelihood of their occurrence in ordinary practice, we have made no study of their action on mercuric chloride paper. One would suppose from analogy, also, that the reactions in small amount would be similar to that of hydrogen sulphide. We note in this connection that Rosenheim <sup>31</sup> states that hydrogen selenide has no influence on the Gutzeit test, unless in large quantity, if lead acetate paper is used.

The results of the above experiments are tabulated for comparison as follows:

### TABLE II.

REACTIONS OF COLOR BANDS WITHIN THE RANGE OF THE ARSENIC STANDARDS FROM APPROXIMATELY EQUIVALENT AMOUNTS OF ARSINE, STIBINE, PHOSPHINE, AND HYDROGEN SULPHIDE.

| Element. | Amounts<br>taken for<br>Reduction.            | Initial<br>Band. | Action of<br>Air.                             | Cold<br>Water.                | Hot<br>Water.                                        | Hydro-<br>chloric<br>Acid. | Auric<br>Chloride.           | Ammonia.              |
|----------|-----------------------------------------------|------------------|-----------------------------------------------|-------------------------------|------------------------------------------------------|----------------------------|------------------------------|-----------------------|
| As       | 30 mmg.<br>(As <sub>2</sub> O <sub>3</sub> ). |                  |                                               | Consid-<br>erably<br>bleached | Grayish<br>white                                     | Dark<br>red                | Bright<br>purple             | Dense<br>black        |
| Sb       | 200 mmg. (Sb <sub>2</sub> $\Omega_3$ ).       |                  | Un-<br>changed                                | Bleached                      | Grayish<br>white                                     | Grayish                    | Dull<br>purple               | Dull<br>blac <b>k</b> |
| Р        | 200 mmg.<br>(P).                              | Pale<br>yellow   | Pale<br>brown<br>where<br>exposed<br>to light | Consid-<br>erably<br>bleached | Faint<br>yellow.                                     | Bright<br>lemon<br>yellow  | Red<br>brown<br>to<br>purple | Gray<br>black         |
| S        | 50 mmg.<br>(S).                               | Dull<br>yellow   | Un-<br>changed                                | Un-<br>changed                | Un-<br>changed.<br>On stand-<br>ing, light<br>brown. | Brighter<br>yellow         | Slightly<br>brown            | Pale<br>brown.        |

<sup>31</sup> Chem. News, 83, 277 (1901).

#### THE PROCEDURE IN PRESENCE OF ARSENIATES.

It is well known that the reduction of an arseniate solution to arsine goes on more slowly than that of an arsenite. This is provided for in the Marsh procedure by continuing the reduction for a longer time when arsenic acid is present; fully an hour, or, if small amounts are present. still longer. The deposition of the mirror being in a comparatively small compass, its size and appearance are not appreciably changed, within the range of the standards, by the slower accumulation of the arsenic particles. In the Gutzeit procedure the case is different for The formation of the color bands is over a greater surface and the standard set is based on the deposition of the color in a short time, which, in turn, depends upon a comparatively quick reduction of the arsenious acid. Not only will some arsenic escape reduction during this time, if arsenic acid is present, but the slower congregation of the particles will result in a shorter band. Hence, from a given amount of arsenic as arseniate, the reading of the color after thirty minutes is invariably low. The subsequent reduction may be studied fractionally for sixty to ninety minutes, with successive strips, although the colors from the last fractions may only be shown by the 2 mm. strips (see The proportion of color within thirty minutes has been shown by us from repeated trials to be reasonably definite. It is rarely over 50 per cent of the standards, rarely under 40 per cent, and the bands formed are somewhat denser in appearance. This implies that the band from an arseniate, though shorter, contains more arsenical substance than a band of the same length from an equivalent amount of arsenite, and this is borne out by the fact that the subsequent color estimations from the continued reduction do not apparently carry the total percentage of arsenic to more than 80.

There are two ways of approximately estimating the value of the color bands derived from arseniates. We may either make a series of standards from known amounts of arsenic as arsenic acid, with which the test band from an arseniate may be compared, or we may multiply the reading of the ordinary standards by 2 or 2.5. Either of these alternatives will answer, more simply the latter, — though both are obviously inexact, — if one's object is only to get a rough idea of the amount of arsenic present. The estimation can be made, however, within the ordinary limits of the method, if the arseniate is converted to arsenite before reduction to arsine.

Before arriving at the procedure finally adopted, we studied the effect on the reduction of an increase of temperature and also that of various catalyzers. A solution containing 10 mmg. of arsenious oxide

as arsenic acid was prepared by evaporating 10 c.c. of solution I repeatedly with nitric acid and making up to one liter. The bottles were heated during the reduction in an air bath in such a way that all above the necks protruded. At 60° the bands obtained from 3 c.c. of the arseniate solution after thirty minutes of reduction were only about 43 per cent of the standard for 30 mmg. of arsenious oxide. Parallel trials with 3 c.c. of the arsenite solution gave bands of the standard length. Another experiment at 90° gave no better results. The bands from the arseniate solution were not over 50 per cent of the standard, while the parallel arsenite reductions gave shorter bands than at ordinary temperature, owing to the larger amount of moisture carried over. That a reduction at the boiling point would cause a practically complete conversion to arsine, as claimed by Bird, seems improbable, while the moisture equilibrium would be so disturbed as to invalidate the procedure.

Returning to the reduction at ordinary temperature, it was found that no increased effect was produced within the standard time by the addition of stannous chloride or potassic iodide. Platinum in contact with the zinc, even when the acid was more concentrated, was of no service, and the use of copper-covered zinc did not help. An appreciable increase but not a complete reduction was effected by sesquisulphate of titanium. It was evident that the use of a catalytic agent did not solve the problem with such small amounts of arsenic, and we were therefore forced to a reduction of the arseniate to arsenite before testing. For this purpose we found sulphurous acid the simplest substance, since comparatively little is needed, no excess of reagent need be left in solution, and it can easily be prepared free from arsenic.

The sulphurous acid solution was made from pure copper and pure sulphuric acid, and was saturated at 0°. The solution gave no test for arsenic when tested in quantities larger than would be used in an analysis. The tests were made after boiling out the sulphur dioxide from the samples.

We tested the efficacy of the sulphurous acid as follows: Four portions of the arsenic acid solution, corresponding to 10, 20, 30, and 40 mmg. of arsenious oxide, were evaporated in small glass dishes with 6 c.c. of the sulphurous acid until the excess of sulphur dioxide was apparently expelled. On adding the residues to the reduction bottles, the color bands came up quickly as in the case of arsenites, and in thirty minutes all the bands were equal to the corresponding standards in length and intensity of color. Subsequent trials conducted similarly confirmed these results. The precaution was taken to use the lead

acetate paper, on which in some cases there was a slight deposit of the sulphide.  $^{32}$ 

In practice, when the solution contains an arseniate, or when the substance has been oxidized, say by nitric acid, one may add a sufficient quantity of sulphurous acid to the entire solution or to the aliquot portion taken for reduction. In analysis No. 9, Table I, we followed the latter plan, adding 10 c.c. of sulphurous acid in two parts, the second after partial evaporation. The excess of sulphur dioxide is then expelled, but the evaporation must not be carried too far, as chlorides, if present, would cause a loss of arsenic. In testing the residues the lead acetate paper should be used.

#### THE ABSOLUTE DELICACY OF THE METHOD.

For most practical purposes the set of standards from 2 to 70 mmg. is sufficient. Amounts of arsenic between 2.0 and 0.5 mmg. can be approximated by the 4 mm. strip, but in studying the limit of delicacy we have allowed the action to take place within a smaller compass. The ordinary strip is cut in two, and these pieces are again divided lengthwise, giving a piece 2 mm. wide and 35 mm. long. This is inserted in a tube of slightly more than 2 mm. in diameter, which is fitted into the usual deposition tube by a washer of rubber tubing. With these small strips a series of standards may be made from 10 mmg, down. The yellow color appears definitely, though of course slightly, from 0.5 mmg. Treated with hydrochloric acid, ammonia, or hydrochloric acid and auric chloride, the indication is much sharper, and from this amount up to 10 mmg, the gradation of the 2 mm, standards is well marked. From 0.3 mmg. the yellow color is exceedingly faint, but development with the reagents brings it out. At 0.2 mmg. the formation of yellow is no longer seen, but treatment with hydrochloric acid gives a faint but definite color, which under the glass is seen to be greater than the effect produced by 0.1 mmg. Development with ammonia or auric chloride is also definite. From 0.08 mmg, a faint fringe of color is visible under the glass after treatment with hydrochloric acid, and the indication is even sharper with ammonia or auric chloride. From 0.05 mmg. no results were obtained. tests were made on two solutions, prepared at different times.

Between 0.05 and 0.08 mmg, is clearly the limit at which we have been able to detect any arsenic by the mercuric chloride paper under the conditions of our method. It is safe to set this limit at 0.08 mmg.

<sup>&</sup>lt;sup>32</sup> We have found that the lead acetate paper is more sensitive to hydrogen sulphide than the mercuric chloride.

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(0.00008 mg.) of arsenious oxide, which is equivalent to 0.00006 mg. of metallic arsenic or one seventeen-thousandth of a milligram.

In the above tests, on quantities under 10 mmg., the hydrochloric acid containing 0.004 mg. arsenious oxide per liter was used. This, in 15 c.c. of the diluted acid, assured a quantity of arsenic far below the above limit, while blank tests of over an hour's duration gave negative results. The deposits from these small amounts were formed within thirty minutes, and each reduction was continued thirty minutes longer.

Although the method is a very delicate one, as shown by the above tests, we are far from claiming that 0.08 mmg. of arsenious oxide can be recognized by it with certainty under the varying conditions of analytical practice. We are not so much concerned with the absolute delicacy, however, as with the amount which may be considered a practical limit, the recognition of which is definite under all conditions, and which, when obtained from an aliquot portion of a solution, may safely be used as a factor in the quantitative determination of the arsenic. In this particular we agree fully with Chapman and Law, 33 who have expressed the opinion that in the Marsh method 5 mmg. should be taken as a practical limit, and that one's efforts should be directed toward recognizing this amount with certainty. We consider. therefore, that 1 mmg. (0.001 mg.) of arsenious oxide may be set as the practical limit of our method, although less than one tenth of this amount may be recognized under favorable conditions. The color produced on the large or small strip by 1 mmg, need not be confused with that from hydrogen sulphide, stibine, or phosphine, if these are unavoidably present, while the more minute traces of color, though not easily confounded with those from the first two, are similar in appearance to that from the last. We have found by trial that 0.1 mmg. of arsenious oxide, if present as arseniate, can be recognized after reduction with sulphurous acid.

Previous estimates of the delicacy of the Gutzeit test have not been under 0.1 mmg., so far as we know, with the exception of that made by Dowzard,<sup>34</sup> who states that one fifteen-thousandth to one twenty-thousandth of a milligram can be recognized by the modification described by him. This figure is practically the same as ours.

# THE USE OF THE METHOD.

The method naturally suggests comparison with the Marsh in the present accepted form of the latter. In the modification described by

<sup>33</sup> Zeits. f. angew. Chem., 20, 67 (1907).

<sup>34</sup> Loc. prim. cit.

one of us (S.) in 1891,35 in which a standard set of mirrors was employed for the first time, the absolute limit of delicacy was placed at 1 mmg. of arsenious oxide. The most important improvement in procedure which has been made of late years is the cooling of the capillary tube, described by Gautier, 36 Thomson, 37 Lockemann, 38 and others. By this means the scattering of the deposit of arsenic is prevented and the mirror takes a more compact and hence more easily identifiable form. In spite of this advantage, we have not been able, as yet, to reach the absolute limit of delicacy in the Marsh process which is set by Thomson at 0.4 mmg. of arsenious oxide, by Lockemann and others at 0.1 mmg. arsenic. We cannot think that this failure is due to insensitiveness of the zinc, but to other reasons not yet discovered. Sanger and Gibson 39 have shown, for example, that the nature of the antimony mirror depends upon the kind of glass tubing used, and they suggest that a greater or less oxidation of the stibine may take place in the accidental presence of air, if the glass contains a catalyzing agent. If this were true, it is easy to imagine a slight retention of the arsenic from the same cause, since the oxide formed would be fixed by the base of the glass. This point will be soon investigated in this laboratory.

Not only, as far as our experience goes, has the Gutzeit method proved to be more sensitive than the Marsh, but we think it will be found so by others. In certain lines of work, in which the sample may be tested directly or quickly freed from interfering substances, the Gutzeit in the form proposed by us may be preferable to the Marsh, particularly when the routine analysis of a large number of samples is concerned. In toxicological or legal work it will serve as a valuable adjunct to the Marsh method, since the exhibits from both methods can be presented and will corroborate each other, qualitatively or quantitatively. Though not convertible, like the Marsh mirror, to a definite and obvious compound of arsenic, yet the color band can be easily differentiated from the effect produced by other substances on mercuric chloride.

We have not studied the application of the method to the analysis of many products, though we have used it successfully for the determination of arsenic in wall paper, in the urine, and in certain salts.

<sup>35</sup> Loc. cit.

<sup>36</sup> Bull. Soc. Chim., 27, 1030 (1902).

<sup>37</sup> Chem. News, 88, 228 (1903); also, 94, 156 and 166 (1906).

<sup>38</sup> Loc. cit.

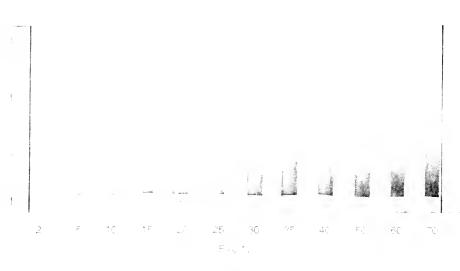
<sup>&</sup>lt;sup>39</sup> These Proceedings, **42**, 719 (1907); Jour. Soc. Chem. Ind., **26**, 585 (1907); Zeits. f. anorg. Chem., **55**, 205 (1907).

Its usefulness will depend upon its adaptability to the needs of the analyst, and it may be modified to meet his conditions. For instance, in the examination of beer, if the analyst must add the sample to the reduction bottle without previous treatment, there should be adequate provision for the retention of hydrogen sulphide, the prevention of frothing, etc. We are not at all sanguine of the success of the method, however, unless the test solution has had adequate treatment before reduction.

During the study of the interference of sulphur, phosphorus, and antimony, as given above, the possibility of quantitatively determining small amounts of these substances by this method, particularly of antimony, suggested itself. We desire to note also that the principle of allowing the gas to be tested to act along the surface of the reacting substance has a useful application in other cases, notably in the determination of fluorine, and we are at present engaged in developing a method for the estimation of small amounts of that substance according to this principle.

In conclusion, it gives us pleasure to acknowledge our indebtedness to the C. M. Warrén Fund of Harvard University for material assistance in the preparation of the colored plates used in this article.

Harvard University, Cambridge, Mass., U. S. A., August, 1907.

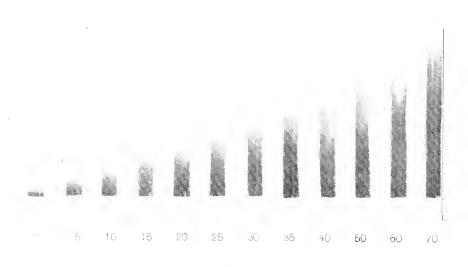




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AMMONIA DIEVELOPMENT.

FROM AMER. ACAD. AFTS AND SCIENCES VOL. LIII.





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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE DETERMINATION OF ARSENIC IN URINE.

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.



# THE DETERMINATION OF ARSENIC IN URINE.

BY CHARLES ROBERT SANGER AND OTIS FISHER BLACK.

Presented January 9, 1907. Received August 20, 1907.

Some years ago one of us (S.) had occasion to make a number of analyses of urine in cases of suspected chronic arsenical poisoning. 1 In looking up the literature of the subject at that time, it was found that the analysis of the urine in case of chronic arsenical poisoning had been comparatively rare. In the twenty-three cases cited by Sanger in which the urine had been examined and the methods of analysis described, the latter were generally open to adverse criticism. They were usually tedious and often involved the use of many reagents, thereby adding to the possibility of introduction of arsenic. The amounts of arsenic found, in the absence at that time of any method for the determination of small quantities, could only be judged from the descriptions of the mirrors, but probably did not exceed 1 mg. of arsenious oxide per liter, and in many cases must have been less than 0.1 mg. In the only analysis found in which quantitative results were given, the amount was stated to have been 16.8 mg. in 1700 c.c., but the method of analysis was not given, hence this case was not included in the twenty-three above mentioned.

The method used by Sanger for the treatment of the urine was based on that proposed by Gautier <sup>2</sup> for the general treatment of animal tissue. To a measured volume of urine was added about one tenth the volume of concentrated nitric acid, and the whole was evaporated over a free flame. As the mass neared dryness the flame was lowered, and more acid was added, if necessary, in order to avoid carbonization at the end. Deflagration often ensued, but it was thought that loss of arsenic should not be feared in presence of excess of nitric acid. To destroy the organic matter completely, the residue from evaporation was transferred to a smaller dish, treated with sulphuric acid, and heated for some time, with addition of nitric acid, until a clear, white, partly melted mass was obtained. The residue, free from nitric acid,

<sup>&</sup>lt;sup>1</sup> These Proceedings, 29, 148 (1894).

<sup>&</sup>lt;sup>2</sup> Ann. d. Chim. et d. Phys, [5] **8**, 384 (1876); Bull. Soc. Chim., [2] **24**, 250 (1875).

was diluted with water and introduced into the Marsh flask. The amount of arsenic was determined by Sanger's <sup>3</sup> modification of the Berzelius-Marsh method.

In the twenty cases of suspected arsenical poisoning referred to in the above paper, thirty-one samples of urine were examined by this method, and in no instance was the amount of arsenic (as arsenious oxide) greater than 0.07 mg. per liter. The analytical precautions were such as to preclude the introduction of arsenic from any outside Prior to these analyses but one instance had been found in which a method for the quantitative estimation of arsenic in urine had been described. Hubbard, 4 in studying the elimination of arsenic by the kidneys, added the urine directly to the Marsh flask and determined the weight of the mirror according to the gravimetric Berzelius-Marsh method, first applied by Gautier,<sup>5</sup> and afterwards elaborated by Chittenden and Donaldson 6 and others. While the amounts of arsenic found by Hubbard (varying from 0.35 to 1.12 mg. per liter) were undoubtedly a close approximation, the method cannot be applied to minimal amounts with certainty on account of the impossibility of accurately weighing small mirrors and the effect of the presence of organic matter on their deposition.

The treatment described above has been used by several analysts 7 in the determination of arsenic in urine. Unfortunately it was not accurately tested by the analysis of urines containing known amounts of arsenic, partly on account of lack of time, partly through acceptance of the Gautier method. The assumption that all of the arsenic present was accounted for was probably incorrect, as our present work will show.

The method is a troublesome one, requiring much time for evaporation and the destruction of the organic matter, as care must be taken to have the latter entirely eliminated, since the accurate determination of the arsenic is impossible in its presence. The use of large quantities of nitric acid is unpleasant and may introduce error. These considerations, together with the much more important one of possible loss of arsenic, have led us to substitute for the destruction of the organic matter with nitric acid a distillation of the arsenic from the evaporated urine by means of hydrochloric acid.

<sup>&</sup>lt;sup>3</sup> These Proceedings, 26, 24 (1891); Amer. Chem. Jour., 13, 431 (1891).

Physician and Surgeon, Ann Arbor, Mich., 4, 348 (1882); Contr. Chem. Lab.
 Univ. Mich., 1, Part 1 (1882).

<sup>&</sup>lt;sup>6</sup> Amer. Chem. Jour., 2, 235 (1881).

<sup>&</sup>lt;sup>7</sup> Putnam-Worcester, Bost. Med. Surg. Jour., **124**, 623 (1891); Wood, Ibid., **128**, 414 (1893); and others.

The distillation of arsenic from organic matter by hydrochloric acid, first used successfully by Schneider <sup>8</sup> and Fyffe, <sup>9</sup> is a common procedure and needs no explanation. We have not been able, however, to find any instance of its application to the analysis of urine. The only serious objection is the difficulty of obtaining hydrochloric acid with a negligible amount of arsenic. Fortunately such an acid is obtainable at low cost in this country, <sup>10</sup> and one does not have to resort to the troublesome methods of purification, which to some are prohibitive of the use of hydrochloric acid in arsenic work.

Not only is the distillation method more accurate, but it will also be shown that, in point of time for the entire operation, the advantage is greatly in its favor, particularly, as we have said before, if the careful elimination of the organic matter is made a prerequisite to the introduction of the solution into the Marsh flask.

#### THE METHOD.

Apparatus. For distillation, a 300 c. c. round-bottom flask is used. with a neck about 20 cm. long. The side tube, which is about halfway up the neck, is 20 cm. in length, and is bent downward in the middle at an obtuse angle, so that it passes into an upright condenser parallel to the neck of the boiling flask, which is closed by a short glass tube sealed off at each end, over which is slipped a short piece of rubber tubing. A glass-stoppered boiling flask could advantageously be used. The cooling tube is 50 cm. long, with a jacket of 35 cm. side tube of the flask passes through a rubber stopper in the neck of the condenser and as far into the cooling tube as possible. The condensing tube passes at the bottom through a rubber stopper, over which is slipped a wide tube 15 cm. long, similar to a chloride of calcium tube, having a bulb of about 25 c.c. capacity near the lower end, which terminates in a tube of ordinary bore. To this end is fused a tube of equal diameter about 15 cm. long. The arrangement is practically a pipette-shaped adapter, similar to that used in ammonia distillation, and is intended to prevent the rise of distillate into the condenser in case of back pressure. The distilling apparatus is conveniently set up in duplicate, mounted on two stands (see Figure A), and is placed in the hood under a strong draught.

Distillation. 200 c.c. of urine are evaporated in a porcelain dish over a low flame or on the steam bath to about 35 c.c., cooled, and in-

<sup>8</sup> Pogg. Ann., 85, 433 (1851).

<sup>&</sup>lt;sup>9</sup> Jour. f. prakt. Chem., **55**, 103 (1852).

<sup>10</sup> Baker and Adamson Chemical Company, Easton, Pa.

troduced into the flask, which is then connected with the condenser. Under the adapter is placed a small flask containing 25 c.c. concentrated nitric acid, which should just cover the end of the adapter. There are then added, through a long funnel tube, 100 c.c cool, con-

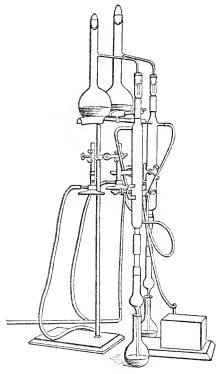


FIGURE A.

centrated hydrochloric acid, in which the amount of arsenic is as small as possible and accurately determined. The stopper of the flask is at once inserted.

Distillation is begun with a low flame and is continued at such a rate that the volume of the liquid in the flask is reduced to about half in the course of thirty to forty minutes. Repeated trials have shown that all the arsenie, in the quantities for which this method is intended, goes over by this operation, whether the arsenic is present as arsenious or arsenic acid. As by far the greater part of the arsenic goes over

with the gaseous hydrochloric acid and meets the concentrated nitric acid, no loss is to be feared from the dilution of the nitric acid by the acid distillate. Comparatively little organic matter is distilled, and this is entirely destroyed by the subsequent procedure.

Treatment of the Distillate. To the distillate are added 25 c.c. concentrated nitric acid, in order to decompose completely during evaporation any excess of hydrochloric acid and thus guard against loss of arsenic. The mixture is then evaporated to a small bulk, three to five cubic centimeters of concentrated sulphuric acid added, and the evaporation continued until the nitric acid is expelled. To destroy the slight amount of organic matter which usually remains, a few drops of nitric acid are added, and the heating is continued until only the small residue of sulphuric acid is left, which must be colorless. The residue is then diluted with water to a measured volume of about 25 c.c., or, if preferred, to a quantity which is weighed in a side-neck test tube to the second decimal place.

Determination of the Arsenic. The subsequent procedure, as in the paper above referred to, follows closely the method of Sanger 11 for determining small amounts of arsenic, except that the capillary tube should be cooled at the deposition point of the mirror, as advised by Gautier, 12 Thomson, 13 Lockemann, 14 and others. An aliquot portion of the ultimate solution, accurately measured or weighed, is introduced into the Marsh flask, the entire apparatus having been in action for a sufficient time to show absence of arsenic. This time varies according to the importance of the test in hand, but should not be less than twenty minutes. If, after the addition of the solution, a mirror does not make its appearance in the capillary tube within ten minutes, a larger portion or the whole of the solution is added. After the appearance of the mirror the heating of the tube is continued for a sufficient time to insure the complete deposition of the arsenic, which usually occurs within an hour. During this time the flow of hydrogen is regulated by the constant generator, so that the height of the flame at the end of the heated tube is about one millimeter, the regular deposition of the mirror being dependent on this condition. The mirror obtained is compared with a set of standards, which is prepared as explained in the paper referred to. From the amount of solution used and the

<sup>11</sup> Loc. cit.

<sup>&</sup>lt;sup>12</sup> Bull. Soc. Chim., [2] **27**, 1030 (1902.)

<sup>13</sup> Chem. News, 88, 228 (1903).

<sup>&</sup>lt;sup>14</sup> Zeitschr. f. angew. Chem., **18**, 416 (1905).

volume of urine taken, the quantity of arsenic per liter is calculated. Should the mirror exceed in size the standard of 0.06 mg., it may be necessary to obtain another mirror from a smaller portion of the solution or from a smaller volume of urine, since the reading of mirrors above 0.06 mg. is not accurate.

The determination of the amount of arsenic in the solution may also be made by the modification of the Gutzeit method described by us in the preceding paper. In this case, owing to the size of reduction flask used, the volume of the solution should not exceed 20 c.c., of which an aliquot part or all may be taken. This method consists briefly in allowing the arsenical hydrogen to pass through a tube containing a strip of paper saturated with a five per cent solution of mercuric chloride and dried. The resulting band of color is compared with a set of standard bands.

Reagents. The zinc used, known as Bertha spelter, from the New Jersey Zinc Company of New York, has been used in this laboratory for many years, and has been exhaustively tested for arsenic with negative results. It contains not over 0.013 per cent of iron and not more than 0.019 per cent of lead. The amount taken is from five to ten grams. We have used it in a rather finely granulated form in the reduction bottle, reserving the larger pieces for the constant generator. As the metal is too pure to generate hydrogen with sufficient rapidity from sulphuric acid, we place in the reduction bottle a thin disk of platinum foil nearly as large as the bottom of the bottle. With this the evolution of the hydrogen is most regular. That the platinum does not cause arsenic to be held back, we have assured ourselves by obtaining mirrors of equal size and same appearance as those formed without the disk. The deposition of platinum on the zinc by use of platinic chloride is, however, not allowable, as one of us has shown, 16 and cupric sulphate is equally inadmissible. The formation of a coating of copper on our zinc, after the procedure of Lockemann, 17 does not add to its sensitiveness, nor does the addition of tin or lead salts to the solution during reduction. In the constant generator, the zinc is sensitized, according to the suggestion of Gooch, 18 by treatment with a solution of cupric sulphate, but we take the precaution to pass the hydrogen from the generator through a ten per cent solution of

<sup>&</sup>lt;sup>15</sup> These Proceedings, **43**, 297 (1907); Jour. Soc. Chem. Ind., Vol. **26** (1907); Zeitschr. f. anorg. Chem., Vol. **56** (1907).

<sup>16</sup> Loc. cit., p. 39.

<sup>17</sup> Loc. cit.

<sup>&</sup>lt;sup>18</sup> Amer. Jour. Science, [3] **48**, 292 (1894).

cupric sulphate in order to retain any hydrogen sulphide which may be formed.

The sulphuric acid is from the Baker and Adamson Chemical Company, and has never shown a trace of arsenic when tested in greater quantity and for a longer time than in a single determination. In the constant generator it is used at a dilution of 1 to 8; in the reduction bottle somewhat more dilute (1.5 normal).

The hydrochloric acid is also obtained of the Baker and Adamson Company. Two grades <sup>19</sup> have been used: the ordinary chemically pure acid (A), which was found by repeated trials to contain 0.4 mg. arsenious oxide per liter; and a second (B), in which we have determined by careful analysis an amount equal to 0.02 mg. per liter.

The nitric acid is an ordinary, chemically pure acid, tested in large quantity after evaporation with sulphuric acid and found to be entirely

free from arsenic, both by the Marsh and Gutzeit tests.

Utensils. All glass and porcelain vessels were new, and, after freedom from arsenic was assured by blank tests, were reserved for this purpose alone.

#### ANALYTICAL RESULTS.

Blank Tests. 1. 100 c.c. hydrochloric acid (A) were diluted with 35 c.c. water and distilled into 25 c.c. nitric acid. From the evaporated distillate a mirror was obtained equal to 0.04 mg. arsenic.<sup>20</sup> Amount per liter, 0.4 mg.

2. 100 c.c. acid (A) were added, drop by drop, to 50 c.c. hot nitric acid in a porcelain dish. The mixture evaporated with sulphuric acid gave a mirror equal to 0.04 mg. arsenic. Amount per liter, 0.4 mg.

- 3. 100 c.c. hydrochloric acid (B) were diluted with 35 c.c. water and distilled into 25 c.c. nitric acid. The evaporated distillate gave a mirror which was judged to be about 0.003 mg. arsenic.
- 4. 200 c.c. acid (B) were added, drop by drop, to 100 c.c. hot nitric acid and the resulting mixture evaporated with sulphuric acid until the nitric acid was expelled. From this was obtained a mirror which was read as 0.002 mg. arsenic.

From analyses 3 and 4 it was evident that there was a trace of

26 In these analyses "arsenic," unless otherwise specified, means arsenious

oxide.

<sup>19</sup> A third grade (C) has been obtained from the same source since the completion of the analytical work on this paper. In this acid, which is of exceptional purity, the amount of arsenic is not over 0.004 mg, per liter.

arsenic in the acid (B), probably about 0.002 mg. in 100 c.c. or

0.02 mg. per liter.

5. 300 c.c. urine were evaporated to 30 c.c. and distilled with 100 c.c. hydrochloric acid (A) into 25 c.c. nitric acid. One half of the solution from the evaporated distillate gave a mirror equal to 0.02 mg. arsenic; the other half, a color band (Gutzeit) equal to 0.02 mg. The amount of arsenic per liter is therefore 0.4 mg., which confirms the results of analyses 1 and 2, and the test shows the urine to be free from arsenic.

6. 200 c.c. urine were evaporated to 30 c.c., and distilled with 100 c.c. acid (B) into 25 c.c. nitric acid. The distillate, evaporated with a little more nitric acid, gave a mirror which, as nearly as could be judged, was equal to 0.002 mg. This confirms, within the limits of reading, the results of analyses 3 and 4, and enables us to fix the correction for 100 c.c. of this acid at 0.002 mg. This has been since confirmed by the analysis of the acid by the Gutzeit method. The correction is only appreciable, as will be seen from Series B, below, when the entire solution gives a very low mirror, and entirely disappears when the mirror, even if a low one, is obtained from a small part of the solution (see Series C).

The third grade of hydrochloric acid (C), which will hereafter be used in all urine work in this laboratory, was tested as in analyses 2 and 4. After reduction of the residues from two lots of 100 c.c. with sulphurous acid, color bands were obtained equal to 0.3 and 0.5 micro-milligrams (0.001 milligram) of arsenic. This is equivalent to 0.004 mg. arsenic per liter. The correction for 100 c.c. of this acid, 0.0004 mg., would be practically inappreciable under ordinary conditions of the Marsh procedure, even if the mirror was obtained from the entire solution.

Analyses. For use in the subsequent analytical work, a solution of arsenious acid was made as follows: One gram of pure arsenious oxide, twice resublimed, was dissolved in a small amount of sodic hydroxide free from arsenic. After acidification with sulphuric acid, this solution was made up to a liter. Of this, 10 c.c. were diluted to a liter, giving a solution containing 0.01 mg. arsenious oxide to the cubic centimeter.

7. 150 c.c. urine, to which had been added 0.025 mg. arsenic, were evaporated to 25 c.c. and distilled with 100 c.c. hydrochloric acid containing 0.035 mg. arsenic. The total amount was 0.06 mg. 25 c.c. of distillate were collected in 25 c.c. nitric acid, and from this was obtained a mirror equal to 0.06 mg. 50 c.c. more of the distillate were collected in 15 c.c. nitric acid, and from this no mirror was found.

- 8. By the same procedure as in analysis 7, and also with 150 c.c. urine, 25 c.c. distillate gave 0.06 mg. arsenic, equal to the amount taken. 50 c.c. additional distillate gave no mirror.
- 9. With 200 c.c. urine and the same amount of arsenic, the same procedure gave 25 c.c. distillate containing 0.06 mg. arsenic, and 50 c.c. additional distillate yielded no further mirror.

The results of analyses 7, 8, and 9 show that by distilling one half the contents of the flask, according to the method above described, all the arsenic passes over.

The following series shows that by the former method of destroying the organic matter by evaporation with nitric acid a very large error is made:

SERIES A.

NITRIC ACID METHOD.

| No. of Analysis. | Volume of Urine taken. | $\mathbf{As}_2\mathbf{O}_3$ added. | $\mathrm{As}_2\mathrm{O}_3$ recovered. | Per cent<br>recovered. |
|------------------|------------------------|------------------------------------|----------------------------------------|------------------------|
|                  | c.c.                   | mg.                                | mg.                                    |                        |
| 10               | 500                    | 250                                | 6.0                                    | 24                     |
| 11               | 500                    | 2.5                                | 0.44                                   | 18                     |
| 12               | 800                    | 0.3                                | 0.00                                   | 0                      |
| 13               | 100                    | 0.5                                | 0.00                                   | 0                      |
|                  |                        |                                    |                                        |                        |

In analyses 10 and 11, actual deflagration took place; in Nos. 12 and 13 the residues were blackened.

The next series, B, p. 336, gives the results of a preliminary trial of the distillation treatment, and shows that by the distillation method very small amounts of arsenic can be recovered with practical completeness. As a more severe test of the method, 0.01 mg. arsenic was added to a liter of urine and the analysis carried out as usual, using acid B (Analysis 39). A mirror was obtained fully equal to the standard for 0.01 mg.

Even with the correction for this acid, we thus recover from 80 to 100 per cent of the amount of arsenic taken, which shows that, considering the amount of organic matter involved and the hydrochloric acid used, the method is a delicate one. By the use of an acid of such purity as that of grade C, it will be possible to eliminate entirely the correction for arsenic in the acid, even if the amount of arsenic in the

SERIES B.

Distillation Method.

| No. of Analysis. | Volume<br>Urine taken. | $\mathbf{A}\mathbf{s}_2\mathbf{O}_3$ added. | $As_2O_3$ in 100 c.c. HCI. | $egin{array}{c} { m Total} \ { m A} arepsilon_2 { m O}_3 \ { m taken.} \end{array}$ | $\mathbf{As_2O_3}$ recovered. | Per cent<br>recovered. |
|------------------|------------------------|---------------------------------------------|----------------------------|-------------------------------------------------------------------------------------|-------------------------------|------------------------|
|                  | c.c.                   | mg.                                         | mg.                        | mg.                                                                                 | mg.                           |                        |
| 16               | 200                    | 0.10                                        | 0.04                       | 0.14                                                                                | 0.14                          | 100                    |
| 17               | "                      | 0.15                                        | "                          | 0.19                                                                                | 0.16                          | 80                     |
| 18               | "                      | 0.05                                        | "                          | 0.09                                                                                | 0.09                          | 100                    |
| 19               | "                      | 0.15                                        | "                          | 0.19                                                                                | 0.16                          | 80                     |
| 20               | "                      | 0.20                                        | "                          | 0.24                                                                                | 0.24                          | 100                    |
| Λvei             | age per cen            | t recovered,                                | Nos. 16 to 2               | 0                                                                                   |                               | . 92                   |
| 38               | "                      | 0.07                                        | 0.002                      | 0.072                                                                               | 0.077                         | 107                    |
| 37               | "                      | 0.06                                        | "                          | 0.062                                                                               | 0.06                          | 97                     |
| 36               | "                      | 0.04                                        | "                          | 0.012                                                                               | 0.04                          | 95                     |
| 35               | "                      | 0.03                                        | "                          | 0.032                                                                               | 0.03                          | 94                     |
| 34               | "                      | 0.02                                        | "                          | 0.022                                                                               | 0.02                          | 91                     |
| 33               | "                      | 0.01                                        | "                          | 0.012                                                                               | 0.01                          | 83                     |
| Aver             | age per cen            | t recovered,                                | Nos. 38 to 3               | 33                                                                                  | :                             | . 95                   |

entire test solution is as low as 0.01 mg., since the correction is only four per cent of this quantity, which is well within the limit of accuracy of the method itself. With larger amounts than 0.01 mg. the correction for this acid is of course of even less account.

Presence of Arseniates in the Urine. The compound in which arsenic occurs in the urine has never to our knowledge been thoroughly investigated. To determine accurately the condition of such small amounts as would ordinarily occur would be a matter of considerable difficulty. Schmidt and Bredtschneider <sup>21</sup> claim to have found arsenic acid and

<sup>&</sup>lt;sup>21</sup> Moleschott's Untersuchungen, 6, 146 (1859).

no arsenious when arsenic was ingested as the trioxide. Selmi <sup>22</sup> states that he found in the urine of a dog poisoned by arsenic a volatile compound of the element. The reference gives no analytical details and the original is not accessible to us. It is not improbable, however, from the analogy to phosphorus, that arsenic finds its way into the urine as an arseniate. If this be the case, the question will perhaps be asked if small amounts of arseniate, when distilled with hydrochloric acid, would be recovered in the distillate or would require a preliminary reduction before distillation.

Mayerhofer <sup>23</sup> has shown that if arsenic acid is distilled with a sufficiently large quantity of hydrochloric acid, it is converted to arsenic trichloride, chlorine being given off, since the pentachloride does not exist under ordinary conditions. In our method the concentration of the hydrochloric acid in 100 c.c. of its solution would be so great compared with that of the arseniate that a complete conversion to trichloride might be predicted. That this is the case is shown by the following analyses, in which the arsenic acid used was prepared by evaporating a measured quantity of arsenious acid solution to dryness with nitric acid before adding to the urine.

SERIES C.

Distillation Method in Presence of Arseniates.

| No. of<br>Analysis. | Volume<br>Urine<br>taken. | $egin{array}{l} As_2O_3 \\ added, \ as \\ H_3AsO_4. \end{array}$ | $As_2O_3$ in 100 e.e. HCl. | Total As <sub>2</sub> O <sub>3</sub><br>taken. | $rac{\mathbf{A} \mathbf{s}_2 \mathbf{O}_3}{\mathbf{recovered}}.$ | Per cent recovered. |
|---------------------|---------------------------|------------------------------------------------------------------|----------------------------|------------------------------------------------|-------------------------------------------------------------------|---------------------|
| 40                  | c.e.<br>200               | mg.<br>0.25                                                      | mg.<br>0.002               | mg.<br>0.252                                   | mg.<br>0.25                                                       | 99.2                |
| 41                  | 66                        | 0.50                                                             | 46                         | 0.502                                          | 0.50                                                              | 99.6                |

Analyses of Urine. The method was finally tested by the analysis of six samples of urine to which varying amounts of arsenic had been added by one of us, the amounts not being known to the analyst.

<sup>&</sup>lt;sup>22</sup> Mem. d. Accad. d. Scienze, Bologna, [4] 1, 299 (1882); ref., Gazz. Chim. Ital., 12, 558 (1882).

<sup>&</sup>lt;sup>23</sup> Ann. Chem. u. Pharm., **158**, 326 (1871).

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SERIES D.

Distillation Method.

| No. of<br>Anal-<br>ysis. | $As_2O_3$ Per Liter. | Volume<br>Urine<br>taken. | As <sub>2</sub> O <sub>3</sub><br>present<br>in<br>Volume<br>taken. | $\begin{array}{c} \text{Total} \\ \text{As}_2\text{O}_3 \\ \text{in} \\ \text{Volume} \\ \text{taken.} \end{array}$ | $egin{array}{c} \mathbf{A} arepsilon_2 \mathbf{O}_3 \\ 	ext{found} \\ 	ext{in} \\ \mathbf{V} olume \\ 	ext{taken.} \end{array}$ | Corrected<br>(Correction,<br>0.04 mg.) | $egin{array}{l} \mathbf{As_2O_3} \\ \mathbf{found} \\ \mathbf{per} \\ \mathbf{Liter.} \end{array}$ | Per<br>cent<br>found. |
|--------------------------|----------------------|---------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|----------------------------------------|----------------------------------------------------------------------------------------------------|-----------------------|
|                          | mg.                  | c.c.                      | mg.                                                                 | mg.                                                                                                                 | nig.                                                                                                                            |                                        | mg.                                                                                                |                       |
| 21                       | 0.5                  | 200                       | 0.10                                                                | 0.14                                                                                                                | 0.15                                                                                                                            | 0.11                                   | 0.55                                                                                               | 110                   |
| 22                       | 2.0                  | "                         | 0.40                                                                | 0.44                                                                                                                | 0.38                                                                                                                            | 0.34                                   | 1.70                                                                                               | 85                    |
| 23                       | 1.0                  | 66                        | 0.20                                                                | 0.24                                                                                                                | 0.23                                                                                                                            | 0.19                                   | 0.95                                                                                               | 95                    |
| 24                       | 1.5                  | "                         | 0.30                                                                | 0.34                                                                                                                | 0.33                                                                                                                            | 0.29                                   | 1.45                                                                                               | 97                    |
| 25                       | 0.8                  | 46                        | 0.16                                                                | 0.20                                                                                                                | 0.17                                                                                                                            | 0.13                                   | 0.65                                                                                               | 81                    |
| 26                       | 1.2                  | 44                        | 0.24                                                                | 0.28                                                                                                                | 0.28                                                                                                                            | 0.24                                   | 1.20                                                                                               | 100                   |
|                          | $\Lambda$ verage     | e per cent                | found .                                                             |                                                                                                                     |                                                                                                                                 |                                        |                                                                                                    | . 93                  |

To show the calculation of the analysis, one example will suffice:

| No. of<br>Analysis. | Volume Urine taken.             | Volume of<br>Solution used. | Volume of<br>Solution taken. | Reading of<br>Mirror. | Reading of<br>Mirror, Average       |
|---------------------|---------------------------------|-----------------------------|------------------------------|-----------------------|-------------------------------------|
| 26                  | e.c.<br>200                     | e.c.<br>50                  | e.c.<br>5                    | mg. a) 0.025          | mg.                                 |
|                     | 200                             | 50                          |                              | b) 0.030              | 0.028                               |
|                     | nt in solution<br>orrection for |                             | 0.028                        |                       | $0.28 \text{ mg}.$ $0.24  ^{\circ}$ |
| Amour               | nt per liter ur                 | ine, $5 \times 0.24$        |                              |                       | . = 1.2 "                           |

Comparison of Methods. In order to compare more fairly the distillation method with the method of evaporation, the latter was slightly modified to secure the most favorable conditions for the recovery of the arsenic. 200 c.c. urine were evaporated to about 50 c.c., and then treated with 25 c.c. concentrated nitric acid and 5 c.c. sulphuric acid. Evaporation was continued until the fumes of sulphuric acid appeared, which left a dark residue containing a large amount of organic matter. By successive addition of small amounts of nitric acid and heating,

this residue was oxidized after a very long time, so that it appeared nearly colorless. The diluted residue was then added to the reduction bottle. A series of analyses was made by this method in which the amounts of arsenic were not known to the analyst.

SERIES E.
NITRIC ACID METHOD, MODIFIED.

| No. of<br>Analysis. | As <sub>2</sub> O <sub>3</sub> per<br>Liter. | Volume<br>Urine taken. | $egin{array}{l} { m As_2O_3} \ { m present} \ { m in \ Volume} \ { m taken.} \end{array}$ | As <sub>2</sub> O <sub>3</sub> found<br>in Volume<br>taken.<br>(Corrected.) | As <sub>2</sub> O <sub>3</sub><br>found per<br>Liter. | Per cent found. |
|---------------------|----------------------------------------------|------------------------|-------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------|-----------------|
|                     | mg.                                          | c.c.                   | mg.                                                                                       | mg.                                                                         | mg.                                                   |                 |
| 27                  | 0.8                                          | 200                    | 0.16                                                                                      | 0.13                                                                        | 0.65                                                  | 81              |
| 28                  | 1.0                                          | "                      | 0.20                                                                                      | 0.08                                                                        | 0.40                                                  | 40              |
| 29                  | 0.5                                          | "                      | 0.10                                                                                      | 0.10                                                                        | 0.50                                                  | 100             |
| 30                  | 2 0                                          |                        | 0.40                                                                                      | 0.24                                                                        | 1.20                                                  | 60              |
| 31                  | 1.2                                          | "                      | 0.24                                                                                      | 0.12                                                                        | 0 60                                                  | 50              |
| 32                  | 1.5                                          | "                      | 0.30                                                                                      | 0.18                                                                        | 0.90                                                  | 60              |
| Αv                  | erage per c                                  | ent found .            |                                                                                           |                                                                             |                                                       | . 65            |

From comparison of Series D and E, it will be seen that the distillation method is more accurate than the evaporation method, even if the latter is carefully conducted so that the loss from carbonization is avoided as far as possible. But the time needed for a proper treatment with nitric acid by the latter method is very great, and the manipulation uncleanly. The entire preparation of the solution for testing, in the distillation method, does not consume more than three fifths of the time required in the other, and the procedure is much cleaner.

#### Use of the Method.

We have not studied the question of how small an amount of arsenic can be recovered from the urine by this method, but have been content to show that very small amounts, even as little as 0.01 mg. per liter, can be detected and estimated with reasonable accuracy. (Series A and Analysis No. 39.) For the examination of abnormal urine, — in studying the elimination of arsenic through the kidneys, for instance, — it would be seldom necessary to consider a quantity

smaller than 0.01 mg., although the delicacy of the Marsh and Gutzeit methods permits a fairly exact estimation of much smaller amounts. If the question of the occurrence of arsenic in normal urine is to be investigated, —and we hope that opportunity for such an important study may be found at some future time in this laboratory, — the delicacy of the methods is secondary in importance to that of the source and manner of collection of the urine. The absolute delicacy of the Marsh method is claimed by Thomson <sup>24</sup> to be 0.0004 mg. of arsenious oxide, by Lockemann <sup>25</sup> and others, 0.0001 mg. arsenic, and we have been able to recognize by our modification of the Gutzeit method as little as 0.00008 mg. of arsenious oxide. But until it is shown that a urine has had absolutely no arsenical contamination, such extreme delicacy is apt to be misleading.

The use of the method in the analysis of other liquids containing organic matter suggests itself, for example in the more exact determination of arsenic in beer. Although the distillation of small quantities of arsenic from animal tissue with hydrochloric acid has been rejected by Lockemann <sup>25</sup> and others, either on account of the amount of arsenic in commercial, pure acid, or the difficulty of purifying the acid, yet we believe that the distillation of organic matter with acid of only 0.004 mg. arsenic to the liter would not introduce a serious error into an investigation of the normal occurrence of arsenic in the organs

of man.

HARVARD UNIVERSITY, CAMBRIDGE, MASS., U. S. A., August, 1907.

<sup>24</sup> Loc. cit.

<sup>25</sup> Loc. cit.

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CONTRIBUTIONS FROM THE FIRST CHEMICAL INSTITUTE OF THE ROYAL FRIEDRICH-WILHELM UNIVERSITY OF BERLIN.

# THE TRANSITION TEMPERATURE OF MANGANOUS CHLORIDE: A NEW FIXED POINT IN THERMOMETRY.

BY THEODORE W. RICHARDS AND FRANZ WREDE.

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# THE TRANSITION TEMPERATURE OF MANGANOUS CHLORIDE: A NEW FIXED POINT IN THERMOMETRY.

BY THEODORE W. RICHARDS AND FRANZ WREDE.

Presented by T. W. Richards. Received October 7, 1907.

In several previous articles one of us <sup>1</sup> has set forth in detail the advantages of the transition temperatures of crystallized salts as fixed points for thermometry. A number of suitable salts have been suggested, and in particular the sulphate and bromide of sodium have been carefully investigated. For these salts the transition temperatures, referred to the international hydrogen scale, have been found to be, respectively, 32.383°C. and 50.674°C.; and both of these salts have been shown to give points constant and definite enough for convenient use for the above-mentioned purpose.

Among the salts studied by Richards and Churchill in an approximate fashion was manganous chloride (MnCl<sub>2</sub>·4H<sub>2</sub>O). This salt has also been investigated roughly by Kuznetzoff, and by Dawson and Williams.<sup>2</sup> All of these investigations were merely approximate; no attempt was made to correct the thermometer for the errors of ordinary thermometry. Therefore they were none of them suitable for defining the point with sufficient exactness for the present purpose. On the other hand all of the investigators agreed in maintaining that the point was constant and definite. Therefore it promises well; and the pres-

<sup>&</sup>lt;sup>1</sup> T. W. Richards, Am. J. Sci. [4], **6**, 201 (1898); Richards and Churchill, These Proceedings, **34**, 10 (1899); Richards and Wells, These Proceedings, **38**, 431 (1902), **41**, 435 (1906). These four papers are all to be found in full in the Zeitschr. für phys. Chem., the references being respectively **26**, 690 (1898); **28**, 313 (1899); **43**, 465 (1903); **56**, 348 (1906). The present paper also will appear in German in that periodical.

<sup>&</sup>lt;sup>2</sup> Kuznetzoff, Chem. Centralblatt, 1899, I, 246; Dawson and Williams, Zeitfür phys. Chem., 31, 59, 1899.

ent paper recites briefly a series of experiments giving much greater definiteness to the point in question and making it available for the verification of thermometers.

#### PREPARATION OF THE MANGANOUS CHLORIDE.

As material for preparation the purest manganous chloride and nitrate of commerce were used. Several preparations made in different

ways assured certainty in the product.

The manganous chloride was purified in the first place by crystallization and centrifugal treatment. Through these processes it was passed four times, after solution in ordinary distilled water, and twice after solution in the purest water. Porcelain and platinum dishes were used. This preparation was called Ia. Two more crystallizations gave Ib, which was found to have essentially the same transition point. Sample Ic was made from the two last mother liquors by further recrystallization. This also gave the same point. During these crystallizations traces of iron were found to exist in the otherwise very pure initial salt; these traces disappeared in the very early stages of the crystallization. This was proved by qualitative tests, which were carefully verified by suitable blank determinations.

The purity of the salt, as indicated by the transition temperature, is shown by the following table. Obviously the transition temperature may be used as a guide concerning the freedom of the salt from everything except isomorphous substances, especially for the present purpose. The crude original substance had a transition temperature of 57.91°: the first fraction, 58.03°; the second, 58.05°; the fourth, 58.072°; the sixth, 58.089°; the eighth, 58.090°; and the ninth, 58.089°.

For the preparation of the chloride from the nitrate of manganese, this nitrate was recrystallized until wholly free from iron. It was precipitated as carbonate by means of redistilled ammonium carbonate. This substance was prepared by distillation with water in a platinum condenser and collected in a platinum dish in which the manganous carbonate was precipitated. The precipitate was boiled with many portions of pure water until no more trace of nitric acid was found in the wash water. It was then dissolved in concentrated pure hydrochloric acid and the chloride was three times recrystallized to eliminate the traces of chlorine due to the excess of nitric acid, and also the traces of hydrochloric acid. The salt gave the same transition temperature as the previous sample, although it had been passed through such different treatment. Therefore it seems reasonable to infer that both samples were pure.

It is perhaps worthy of note that manganous chloride has been found by Kahlenberg, Davis, and Fowler 3 to be only very slightly hydrolyzed at 56°, a temperature very near the transition temperature, 58°. The hydrolysis at this temperature is not enough to cause, during the time of the transition experiment, any considerable chance for the formation of the higher oxides of manganese by action of the air on the slightly hydrolyzed solution. This is of course particularly true of the highly concentrated saturated solution at 58°.

#### DETERMINATION OF TRANSITION TEMPERATURE.

Great care was taken in this work. Besides common thermometers for the determination of the temperature of the thermostat, etc., three instruments of great precision were used.

These were as follows:

- 1. Normal thermometer (of Jena glass, 59<sup>III</sup>) about 48 cm. long. The scale of this thermometer extended from 0° to 100° with bulbs between 5° and 18°, and between 65° and 95°. This instrument was made by Richter of Berlin especially for this determination, and was used in the preliminary experiments which were made to show the constancy point of the purest salt. The results are given in the sixth column of Table I. An accident to the thermometer prevented its exact calibration, but its results are exact relatively to one another, and in this respect are just as good as if this calibration had been carried out.
- 2. A Beckmann thermometer, No. 30, Richter (Jena glass, No. 59<sup>III</sup>). This thermometer was somewhat larger than usual and made with great care. Its column showed an unusually slight tendency to adhere to the glass, and gave, as will be seen, extraordinarily constant readings. The scale was divided into one-hundredths. All determinations made with the other thermometers were also made with this instrument, which thus served as a means of comparing and controlling The results are given in the Tables. The particular point in question, 0.508° on this scale, was standardized with great care by the Physikalisch-Technischen Reichsanstalt and found to correspond to the temperature 58.090° on the international standard. After it had been standardized, the same thermometer was used again for determining the transition temperature, and gave the same results, thus showing that the mercury in the bulb had remained constant in amount under the very careful treatment which it had received.

On account of the breaking of thermometer 1, we desired to confirm

<sup>3</sup> Kahlenberg, Davis, and Fowler, J. Am. Chem. Soc., 21, 1, 1899.

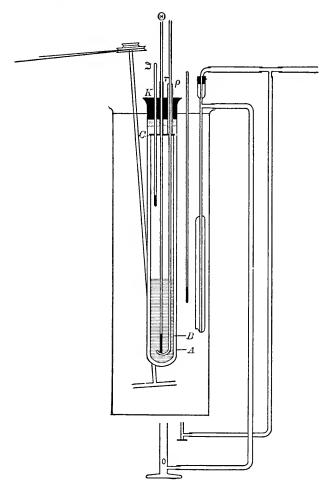
the results of the Beckmann instrument with another carefully standardized normal thermometer which had been directly compared with the standard of the Reichsanstalt. Accordingly another one was procured.

3. Normal thermometer No. 512, Richter (Jena glass, 59<sup>th</sup>). This thermometer was 65.5 cm. long; the whole scale between 0° and 100° was divided into one-tenth degrees. The scale itself had a length of 57 cm. This instrument was tested with the greatest care in the Reichsanstalt, not only as regards its calibration and behavior under pressure, but also as regards the exact position of particular points, especially the point 59.090°. This was found to read upon this thermometer 58.330°, referred to the hydrogen standard, after correction for the ice point and for external pressure; the error here being +0.240°.

The observed values for the transition point in question, determined with the third thermometer, and also the correction for the temperature of the thread, external pressure, and position of the ice point, are to be found in Table II. Further, in that table are given the exact temperature computed in terms of the hydrogen scale, and also the control determinations made simultaneously with the Beckmann thermometer. The errors of the small extra thermometers for the thermostat, etc., were also carefully determined at this point in their scales.

In order to carry out the determination of the transition temperature with a mercury thermometer, it is necessary to have the stem of the thermometer at the same temperature as the bulb. With high temperature the error, due to neglect of this precaution, may be very great. In determining a transition temperature, it is impracticable to immerse the whole thermometer in the melting mixture; therefore some other device is necessary in order to maintain the thread of the thermometer at the right temperature. In the past we have used two devices for this purpose. In one case the thermometer was surrounded by a glass tube, through which circulated water of the right temperature. This device works very well, except that it is difficult to prevent cooling of the water. The other device consisted in a deep thermostat, above which the thermometer just projected. In the present series of determinations we have altered this latter arrangement by making the thermostat of glass, using a very tall glass beaker 52 centimeters in height and 14 centimeters in diameter, surrounded at the sides with asbestos paper and with long narrow windows in front and behind for observation. A sketch of this apparatus is given in the accompanying diagram. Into the water was immersed, quite to its top, a strong, very large tube (A) closed below, of about 5 centimeters diameter. In this there was contained, isolated by pieces of cork, the slightly smaller

tube (B) designed to contain the substance. This tube, and also the stirrer, were made out of good insoluble glass. Because the mercury-thread, which we needed to consider, was 2 centimeters shorter than



the second tube, it was contained entirely within it when the thermometer was raised about a centimeter above the bottom of the tube. This inner tube was closed by a cork cover (C), which was bound by means of two small glass tubes ( $\tau$  and  $\rho$ ) to the cork stopper (K) of the outer tube. The two little tubes binding these two pieces of cork

served to admit the thermometer (9) and the stirrer. The temperature in the outer very large tube fluctuated but very slightly, and that in the inner tube containing the substance was almost exactly con-There was no difficulty in regulating the heat of the water in the thermostat to within less than one tenth of a degree by an ordinary gas regulator. For reading the thermometer (0), a telescope with a very exact micrometer was used, by means of which the smallest scale divisions could easily be divided into hundredths. The danger of irregular readings of the thermometer through the various media, which might cause errors due to parallax, was wholly overcome, in that on the one hand all the glass walls were arranged as vertically as possible. and the telescope was made exactly horizontal, and on the other hand every reading of the thermometer was made both from before and from behind. Obviously, the mean of these two readings must represent the true value, even if a slight displacement due to refraction had been present. The thermometer was so arranged that it could easily be turned on a vertical axis, so that there was no difficulty in making these readings. As a matter of fact, the readings before and behind never differed more than four thousandths of a degree, and usually The true value was always taken as the differed much less than that. mean of these readings. In the case of the Beckmann thermometer, the telescope was so placed that the scale division lines appeared perfectly straight through the tube, without a trace of bending.

The concordance of the results furnishes yet another proof that these methods of reading were entirely satisfactory and thoroughly trustworthy. The great advantage of this apparatus is that the temperature of the scale can be kept indefinitely at a temperature as nearly as possible to the true value, and this is no small advantage, because with such a length of thread a single tenth of a degree difference of temperature causes a thread-correction of  $\frac{1}{1000}$ °. We conclusively proved that it was not possible to attain the necessary constancy if even a millimeter of the mercury thread projected beyond the thermostat into the temperature of the room.

As has been said, in Table I the accurate results with the first thermometer and the Beckmann are given, and also the corrections, in so far as these could be determined. The final determinations with the large new thermometer are given in Table II. On the basis of these results, we think it is safe to say that the transition temperature of manganous chloride for the transition from the crystal form with 4 molecules of water into that with 2 of water, has a value  $58.089^{\circ}$  ( $\pm 0.005$ ) referred to the international hydrogen scale.

In conclusion, it is a great pleasure to express our thanks to the

TABLE I.

|                                    |                      |         |           |                       |                                                    | T                                           |                          | 1                                                                            |
|------------------------------------|----------------------|---------|-----------|-----------------------|----------------------------------------------------|---------------------------------------------|--------------------------|------------------------------------------------------------------------------|
|                                    |                      | The     | ermome    | ter I.                |                                                    |                                             |                          |                                                                              |
| Preparation<br>No.                 | Observed<br>Reading. | Corre   | ection (1 | - <del>1</del> 000°). | Result not<br>corrected<br>to H <sub>2</sub> Stan- | Reading of<br>Beckmann<br>Thermom-<br>eter. | Cor-<br>rected<br>Press. | Result cor-<br>rected to H <sub>2</sub><br>Standard<br>(Reichs-<br>anstalt). |
|                                    |                      | Thread. | Ice.      | Press.                | dard.                                              |                                             |                          |                                                                              |
| Ιa                                 | 58.087               | -2      | 0         | -1                    | 58.084                                             | 0.5078                                      | -1                       | 58.089°                                                                      |
|                                    | 58.081               | -2      | +3        | -1                    | 58.081                                             |                                             |                          |                                                                              |
|                                    | 58.077               | -2      | +5        | -1                    | 58.079                                             |                                             |                          |                                                                              |
|                                    | 58.077               | -2      | +7        | -1                    | 58.081                                             |                                             |                          |                                                                              |
|                                    |                      |         |           |                       | 58.081                                             |                                             |                          |                                                                              |
| Ib                                 | 58.084               | -1      | 0         | -2                    | 58.081                                             | 0.5079                                      |                          | 58.088                                                                       |
|                                    | 58.084               | -1      | 0         | -2                    | 58.081                                             |                                             |                          |                                                                              |
|                                    | 58.085               | -2      | +3        | -2                    | 58 084                                             |                                             |                          |                                                                              |
|                                    |                      |         |           |                       | 58.082                                             |                                             |                          |                                                                              |
| $I_c$                              | 58 077               |         | +5        | -2                    | 58.078                                             | 0.5081                                      |                          | 58 089                                                                       |
|                                    | 58.081               | -1      | +5        | -2                    | 58.082                                             | 0.5082                                      | -1                       | 58.089                                                                       |
|                                    | 58.083               | -1      | +3        | -2                    | 58.083                                             |                                             |                          |                                                                              |
|                                    |                      |         |           |                       | 58.081                                             |                                             |                          |                                                                              |
| II                                 | 58.089               | -5      | +3        | -2                    | 58.085                                             | 0.5075                                      | -1                       | 58.089                                                                       |
|                                    | 58.089               | -4      | +3        | -2                    | 58.086                                             |                                             |                          |                                                                              |
|                                    |                      |         |           | TAB                   | LE II.                                             | <u></u>                                     |                          |                                                                              |
|                                    |                      | New ?   | Thermo    | meter.                |                                                    |                                             |                          |                                                                              |
| $\mathbf{I}b\mathbf{+}\mathbf{I}c$ | 58.334               | -2      | +3        | -2                    | 58.332                                             |                                             |                          |                                                                              |
| +11                                | 58.330               | -0      |           |                       |                                                    |                                             |                          |                                                                              |
|                                    | 58.334               | -6      | _         |                       | 58.329                                             |                                             |                          |                                                                              |
|                                    | 58.330               | -2      | +3        | -2                    |                                                    | 0.5072°                                     | -1                       | 58.088                                                                       |
|                                    |                      |         |           | !                     | 58.331                                             |                                             |                          |                                                                              |
|                                    |                      |         |           |                       | = 58.091°                                          |                                             |                          |                                                                              |
| Ib                                 | 58.324               | -0      | +7        | -1                    | 58 330<br>= 58.090°                                | 0.5076°                                     | -1                       | 58.089                                                                       |
|                                    |                      |         | Total     |                       | 58.0                                               | )890                                        | ···'                     |                                                                              |
|                                    |                      |         |           |                       |                                                    |                                             |                          |                                                                              |

Director of the laboratory, Professor Emil Fischer, and to the President of the Physikalisch-Technischen Reichsanstalt, Professor Warburg, for their interest in and support of this investigation, and to Dr. Grützmacher of the Reichsanstalt for his prompt and thorough testing of our thermometer.

#### SUMMARY.

- 1. For the transition temperature of manganous chloride from the tetrahydrate to the dihydrate the point 58.089° upon the international hydrogen scale has been found. This point is probably not more than 0.005 degree in error.
- 2. This transition temperature of manganous chloride was found to be suitable for serving as a fixed point in thermometry, on account of the ease of preparation of the salt and the satisfactory definiteness of the transition.
- 3. In this paper is described a tall transparent thermostat which makes it possible to determine exactly the temperature of the whole length of the thermometer.

FIRST CHEMICAL INSTITUTE OF THE UNIVERSITY OF BERLIN, August 1, 1907.





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## DIFFERENCE IN WAVE-LENGTHS OF TITANIUM λλ 3900 AND 3913 IN ARC AND SPARK.

BY NORTON A. KENT AND ALFRED H. AVERY.

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# DIFFERENCE IN WAVE-LENGTHS OF TITANIUM λλ 3900 AND 3913 IN ARC AND SPARK.

BY NORTON A. KENT AND ALFRED H. AVERY.

Presented by J. Trowbridge October 9, 1907. Received October 9, 1907.

In June, 1905, one of the writers of the present paper published the results of a careful series of experiments dealing with the variation in the wave-length of certain lines of the spark spectra of titanium, iron, and zinc with the electrical conditions of the discharge. Subsequently Keller, working under Kayser, published a paper in which the suggestion was made that the apparent non-coincidences of the spark and the comparison are lines were due to the fact that the slit was not accurately adjusted to parallelism with the grating ruling; and the statement was made that the plumb-line method of adjustment employed by the writer was of less delicacy than the spectroscopic.

The substance of Keller's explanation of the manner in which shifts could be introduced by orientation of the spectrometer slit is as follows: Given a perpendicular grating ruling, an astigmatic instrument such as the concave grating will give a perpendicular line image for every point of the line source as object. If, then, the line source or slit be at an angle (say clockwise as one faces it) with the grating ruling, each spectral line will be a composite of lines arranged as in Figure 1.

The result will be an image which is apparently rotated in the direction of the slit. If, then, on one photographic plate two exposures be made, one each of arc and spark, and the position of the adjacent tips of the images of any spectral line be measured by a comparator, any displacement desired may be introduced by a rotation of the slit.

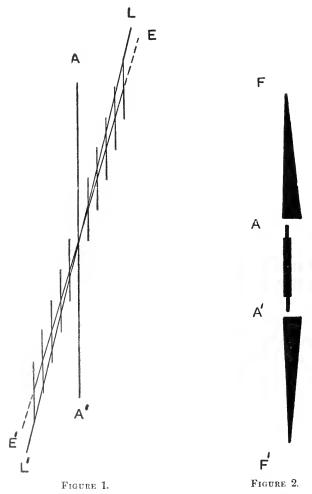
But Keller's explanation does not apply to the method of exposure employed by the writer of the former paper—a method of triple exposure, two of the arc (the first and the third) superimposed horizontally but not wholly vertically and spanned by the spark exposure, as in Figure 2.

<sup>&</sup>lt;sup>1</sup> These Proceedings, **41**, No. 10, July, 1905.

<sup>&</sup>lt;sup>2</sup> Ueber die angebliche Verschiebung der Funkenlinien. Inaugural-Dissertation Christian Keller. 1906.

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It is difficult to see how non-parallelism of slit and ruling could in this case introduce a shift. Keller seems to have overlooked the fact



AA', direction of grating ruling; EE', direction of slit; LL', direction of resultant line.

AA', two exposures of an arc line superimposed horizontally, but not vertically; FF', spark line.

that this triple method was employed, for no mention is made of it in his paper. However, despite the fact that it was not apparent how the above mentioned criticism could apply, it seemed advisable to test the matter, and the following experiments were undertaken to decide the two following questions:

- (1) Is the plumb-line method of adjustment of slit and grating ruling to parallelism more or less accurate than the spectroscopic?
- (2) Will an orientation of the slit introduce a shift if the triple method of exposure be used?

#### CONDITIONS OF EXPERIMENT.

The conditions under which the present work was carried on were, as far as possible, those of the previous series of experiments. courtesy of Professor Trowbridge and Professor Sabine every facility of the Jefferson Physical Laboratory was placed at our disposal. grating — a 6" Rowland concave, of 20,000 lines to the inch and 21-foot radius of curvature, an excellent instrument - was kindly loaned by Professor Trowbridge, and the mount was that belonging to the laboratory and located on the third story of the building. The beams were heavy timbers supported wholly from the walls of the building. slit, grating holder, camera-box, rheostat, transformer, and condenser were those used in the former work. The usual precautions relative to temperature changes were taken, the whole mount being wrapped in several layers of newspaper. The vibrations of the building due to wind and heavy machinery necessitated working at times when these disturbing influences were absent. All plates not showing horizontal coincidence of the arc exposures were rejected. The current used for both arc and spark was the 110 volt, 66 cycle alternating current of the Cambridge Electric Light Company. The frequency of the current used in the previous work was 133, but as the transformer was built for 66 cycles no difficulty was experienced in this regard. The voltmeter, ammeter, and wattmeter were of Thompson form, and of ranges 0-65 volts; 0-60 amperes; and 0-45 hecto-watts, respectively. Thus the conditions were the same as those formerly employed in all respects but location, frequency of current, and grating.

#### RESULTS OBTAINED.

(1) Relative merits of plumb-line and spectroscopic methods of adjustment. The grating holder was fitted with two opposing screws moving in a horizontal direction and controlling the orientation of the grating. It was found by trial that by the unaided eye the parallelism of either end of the ruled space of the grating with the silk thread of a plumbline suspended from the grating holder could be adjusted so that the

#### TABLE I.

Shift of spark lines  $\lambda\lambda$  3900 and 3913 to red from position of arc lines. Metal used Titanium Carbide, 85 per cent Ti, 15 per cent C. Arc vertical: length 3 mm. Spark horizontal: length 9 mm. End of spark image always used. Capacity of condenser: 0.0226 microfarads. Times of exposures: arc 5 + 5 seconds, spark 75 seconds.

|               |           | Con                 | stants            | of                                           |              |        |              |                  |           |                  |                                                | SHIFT IN          |
|---------------|-----------|---------------------|-------------------|----------------------------------------------|--------------|--------|--------------|------------------|-----------|------------------|------------------------------------------------|-------------------|
| er.           |           |                     | ary Cir           |                                              |              |        |              | λ 39             | 00.68     |                  |                                                |                   |
| unn           | Date.     |                     |                   |                                              |              |        | (            | )rientati        | on of Sli | t.               |                                                |                   |
| Plate Number. | Date.     | Amperes.            | Watts.            | Volts.                                       | Clock<br>360 |        | Clock<br>180 |                  | Parallel  | l, or 0°.        | Counte<br>wise                                 | r clock-<br>180°. |
| -             |           | Ā                   |                   |                                              | Kent.        | Avery. | Kent.        | Avery.           | Kent.     | Avery.           | Kent.                                          | Avery.            |
| 19            | Mar. 9    |                     |                   |                                              | 0.035        | 0.041  |              |                  |           |                  |                                                |                   |
| 20            |           |                     |                   |                                              | 0.021        | 0.031  |              |                  |           |                  |                                                |                   |
| 21            |           |                     |                   |                                              |              |        |              |                  | • •       | • •              |                                                |                   |
| 22            | 24        | 40.0                |                   | 15.5                                         | • •          |        |              | • •              |           |                  |                                                | • •               |
| 23<br>26      | Mar. 16   | $ 40.8  \ 42.0$     |                   | 15.5<br>15.5                                 | • •          | • • •  |              | • •              |           |                  |                                                |                   |
| 32            |           | 38.5                |                   | 19.0                                         |              |        |              |                  | 0.019     | 0.023            |                                                |                   |
| 35            |           | 40.0                |                   | 16.5                                         |              |        | 0.020        | 0.027            | 0.010     | 0.020            |                                                |                   |
| 36            |           | 40.0                |                   | 16.5                                         |              |        | 0.012        | 0.022            |           |                  |                                                |                   |
| 39            |           | 39.0                |                   | 21.0                                         |              |        |              |                  | 0.027     | 0.028            |                                                |                   |
| 40            |           | 40.5                |                   | 17.0                                         |              |        |              |                  | 0.007     | 0.013            | 1                                              |                   |
| 44            | Mar. 23   | 39.8                |                   | 19.0                                         |              |        |              |                  | 0.029     | 0.030            |                                                |                   |
| 45            |           | 40.0                |                   | 19.0                                         |              |        | • •          |                  | 0.025     | 0.021            |                                                |                   |
| 48            |           | 37.5                |                   | 21.5                                         | ٠.           | • •    | 0015         | مننما            | 0.018     | 0.018            |                                                |                   |
| 49<br>51      |           | 40.0<br>39.3        | • •               | 18.0<br>18.0                                 | • •          |        | 0.015        | $0.020 \\ 0.013$ |           | • •              |                                                |                   |
| 52            |           | 39.0                |                   | 19.0                                         | 0.032        | 0.042  | 0.014        | 0.015            | ::        |                  |                                                |                   |
| 54            | ::        | 40.0                |                   | 18.8                                         | 0.016        | 0.023  |              |                  |           | ::               |                                                |                   |
| 58            |           | 40.0                |                   | 19.3                                         | 0.010        |        |              |                  |           |                  |                                                |                   |
| 63            | Apr. 12   | 41.0                | 500               | 16.0                                         |              |        |              |                  | 0.014     | 0.018            |                                                |                   |
| 68            | i 13      | 39.0                | 500               | 19.0                                         |              |        |              |                  | 0.008     | 0.010            |                                                |                   |
| 72            |           | 40.0                | 490               | 17.5                                         |              |        |              |                  | 0.023     | 0.023            |                                                |                   |
| 74            |           | 39.5                | 450               | 17.5                                         |              |        |              |                  | 0.039     | 0.029            | 0 005                                          | 0.010             |
| 76<br>77      |           | 40.0                | 500               | $\begin{vmatrix} 22.0 \\ 19.0 \end{vmatrix}$ |              |        |              |                  | • •       |                  | $\begin{bmatrix} 0.025 \\ 0.016 \end{bmatrix}$ | 0.019             |
| 78            |           | 40.0                | 450<br>450        | 19.0                                         |              |        |              |                  |           |                  | 0.010                                          | 0.010             |
| 82            |           | 40.0                | 500               | 19.0                                         |              | ٠.     |              | 1 ::             |           |                  | 0.002                                          | 0.042             |
| 83            | 1         | 41.0                | 450               | 15.0                                         |              |        | ::           |                  |           |                  | 0.025                                          | 0.026             |
| 85            |           | 40.5                | 490               | 17.0                                         | ::           |        | 0.020        | 0 018            |           |                  |                                                |                   |
| 87            |           | 41.0                | 450               | 16.5                                         |              |        | 0.020        | 0.021            |           |                  |                                                |                   |
| 88            |           | 41.0                | 450               | 16.0                                         | 0.025        | 0.021  |              |                  |           |                  |                                                |                   |
| 89            |           | 40.5                | 450               | 16.0                                         | 0.018        | 0.026  |              |                  |           |                  |                                                |                   |
| 101           | Apr. 27   | 40.0                | 450               | 17.0                                         |              |        |              |                  | • •       |                  | 0.008                                          | 0.012             |
| 102<br>110    | • •       | 39.0<br>41.0        | 450<br>450        | 19.0<br>19.0                                 |              |        | • • •        |                  | • •       | • •              | 0.011                                          | 0.009             |
| 1112          |           | $\frac{41.0}{42.5}$ | 450               | 15.0                                         |              |        |              |                  |           |                  |                                                |                   |
| 1114          |           | 41.0                | 450               | 15.5                                         |              | ::     |              |                  |           |                  |                                                | ::                |
| 116           |           | 41.0                | 550               | 19.0                                         |              |        |              | ::               |           | !!               | 0.014                                          | 0.019             |
| 117           |           | 41.8                | 550               | 18.5                                         |              |        |              |                  |           |                  | 0.018                                          | 0.016             |
| 119           |           | 41.5                | 520               | 19.5                                         |              |        | 0.015        | 0.018            |           |                  |                                                |                   |
| 120           |           | 42.0                | 480               | 17.5                                         |              |        | 0.013        | 0.022            |           |                  |                                                |                   |
| 122           |           | 41.3                | 500               | 19.0                                         | 0.014        | 0.014  |              | ٠.               |           | • •              | • •                                            |                   |
| 123<br>124    |           | 41.3                | $\frac{500}{500}$ | 17.0                                         | 0.013        | 0.012  |              |                  | • •       | • •              | • •                                            | • •               |
| 124           |           | 41.5                | 1 900             | 17.0                                         | 0.011        | 0.010  |              |                  |           |                  |                                                |                   |
|               | Mean      |                     | •                 |                                              | 0.021        | 0.024  | 0.016        | 0.020            | 0.021     | 0.021            | 0.019                                          | 0 019             |
|               | eans of n | neans               | at all            | orier                                        | itations     |        |              |                  |           | λ 3900.<br>0 018 |                                                | 3913.58<br>0 017  |
|               | verv .    |                     | : :               |                                              |              |        |              |                  |           | 0.020            |                                                | 0 017             |
| L.,           |           | • •                 |                   |                                              |              |        |              |                  | • 1       | 0.020            | 1                                              | 0 010             |

#### TABLE I - continued.

Plates: Seed "Gilt Edge," No. 27. Developer: Metol, adurol, hydrochinon. Second order spectrum. Width of slit: 0 025 to 0.050 mm.; length: 5 mm. Length of grating lines: 14 mm.

|                 |         |              |         |         |        | λ 391      | 3.58.      |       |                   |        |                   |
|-----------------|---------|--------------|---------|---------|--------|------------|------------|-------|-------------------|--------|-------------------|
|                 |         |              |         |         | (      | Prientatio | on of Slit | 5.    |                   |        |                   |
| Counter<br>wise |         | Clock<br>360 |         |         | wise   | Paralle    | , or 0°.   |       | r clock-<br>180°. | Counte | r clock-<br>360°. |
| Kent.           | Avery.  | Kent.        | Avery.  | Kent.   | Avery. | Kent.      | Avery.     | Kent. | Avery.            | Kent.  | Avery.            |
|                 |         | 0.030        | 0.035   |         |        |            |            |       |                   |        |                   |
|                 |         | 0.018        | 0.028   |         |        | • •        |            |       |                   |        |                   |
| 0.012           | 0.012   |              |         | • •     | • •    | • •        |            |       |                   | 0.014  | 0.013             |
| 0.029           | 0.034   | • •          | ••      |         |        | • •        | • • •      |       | • •               | 0.027  | 0.040             |
| 0 010           | 0.023   |              | ••      | • •     | • •    |            | • •        |       |                   | 0.011  | 0.013             |
| 0.006           | 0.020   |              |         |         |        | 0015       | 0.017      |       |                   | 0.008  | 0.016             |
| • •             |         |              | • •     | 0.000   | 0.000  | 0.015      | 0.017      | • •   | • •               |        |                   |
|                 | • •     |              | • •     | 0.026   | 0.022  |            |            |       |                   |        |                   |
|                 | • •     |              | • •     | 0.010   | 0.019  | 0.000      | 0.004      |       | • •               | • •    |                   |
|                 |         |              |         |         |        | 0.023      | 0.024      |       |                   | • •    |                   |
|                 |         |              | • •     |         |        | 0.004      | 0.012      | ٠.    |                   | • •    |                   |
|                 | • •     | • •          | • •     |         | • •    | 0 029      | 0 033      |       |                   | • •    |                   |
|                 | ••      |              | • •     | 1       |        | 0.021      | 0.029      |       | ••                | • •    |                   |
|                 |         |              |         |         |        | 0.014      | 0.017      |       | • •               | • •    |                   |
|                 | ••      |              |         | 0.018   | 0.017  |            |            | ٠.    |                   |        |                   |
|                 | ••      | 0.001        | 0000    | 0.015   | 0.015  | • •        | • •        |       |                   |        |                   |
|                 | • •     | 0.031        | 0.026   |         |        |            | • •        |       | • •               |        |                   |
| 0.01.           |         | 0.016        | 0.020   |         |        |            |            |       | • •               | 0000   |                   |
| 0.012           | 0.016   | • •          |         |         |        |            | A          | • •   |                   | 0.015  | 0.015             |
|                 | • •     |              | • •     |         | • •    | 0.016      | 0.017      | • •   | • •               |        |                   |
|                 | ••      |              | • •     |         | • •    | 0 005      | 0.005      |       | • •               |        |                   |
|                 |         |              | • •     |         |        | 0.023      | 0.025      |       |                   |        |                   |
|                 | • •     |              |         |         |        | 0.042      | 0.034      |       |                   |        |                   |
|                 |         |              | • •     |         |        |            |            | 0.024 | 0 029             |        |                   |
|                 |         |              |         |         |        |            |            | 0.016 | 0.008             |        |                   |
|                 |         |              |         |         |        |            |            | 0.032 | 0.027             |        |                   |
| 0.028           | 0.023   |              |         |         |        |            |            |       |                   | 0.024  | 0.022             |
|                 |         |              |         |         |        |            |            | 0.020 | 0.018             |        |                   |
|                 |         |              |         | 0.019   | 0.024  |            |            |       |                   |        |                   |
|                 |         |              |         | 0.016   | 0.020  |            |            |       |                   |        |                   |
|                 |         | 0.018        | 0.012   |         |        |            |            |       |                   |        |                   |
|                 |         | 0.021        | 0.023   |         |        |            |            |       |                   |        |                   |
|                 |         |              |         |         |        |            |            | 0 006 | 0.019             |        |                   |
|                 |         |              |         |         |        |            |            | 0.014 | 0.014             |        |                   |
| 0.012           | 0.007   |              |         |         |        |            |            |       |                   | 0 012  | 0.008             |
| 0.015           | 0.009   |              |         |         |        |            |            |       |                   | 0.014  | 0.012             |
| 0.014           | 0.011   |              |         |         |        |            |            |       |                   | 0.013  | 0.014             |
|                 |         |              |         |         |        |            |            | 0.013 | 0.010             |        |                   |
|                 | '       |              |         |         |        |            |            | 0.015 | 0.010             |        |                   |
|                 |         |              |         | 0 016   | 0.025  |            |            |       |                   |        |                   |
|                 |         |              |         | 0.013   | 0 018  |            |            |       |                   |        |                   |
|                 |         | 0.012        | 0 012   |         |        |            |            |       | 1                 |        |                   |
|                 |         | 0.012        | 0.016   |         |        |            |            |       |                   |        |                   |
|                 |         | 0.007        | 0 014   |         |        | II         | ١          |       | l                 |        |                   |
|                 |         |              | -       |         |        |            |            |       |                   |        |                   |
| 0.015           | 0 017   | 0.018        | 0.021   | 0.017   | 0.020  | 0.019      | 0 021      | 0.018 | 0.017             | 0.015  | 0.017             |
| Weigh           | ited me | ans of       | all me  | asurem  | ents . |            |            |       |                   | 0.019  | 0.018             |
| Weigh           | ited me | ans at       | paralle | elism . |        |            |            |       |                   | 0.021  | 0.020             |
|                 | as giv  |              |         |         |        |            |            |       |                   | 0.019  | 0.018             |

separate settings made by each of us agreed to within 45° on the head of one of the screws. This means that the grating can be set by plumb-line to within 3.3 minutes of arc.

Opening the slit and hanging the bob so that the thread could be seen through it, the various settings made by each of us agreed to 10° on a divided head fitted to the tangent screw. This means by calculation 1.7 minutes of arc of rotation of the slit.

On the other hand, using full length of slit, as in the previous case, and appropriate width, about 1/1000 inch, various exposures of the arc were taken on the same plate in the manner customary in making focus plates, except that the camera box was left clamped and the slit was oriented. Plates so taken showed no difference in the spectra when the scale on the divided head of the tangent screw was rotated 90° clockwise or counter clockwise from the position of parallelism as determined by plumb-line, making a change of 15.3 minutes in the orientation of the slit—a change nine times as great as that in the case of the plumb-line. However, the relative merits of the two methods must not be taken as nine to one, but merely as about four to one, for the plumb-line adjustment for the grating is only about one half as accurate as that for the slit.

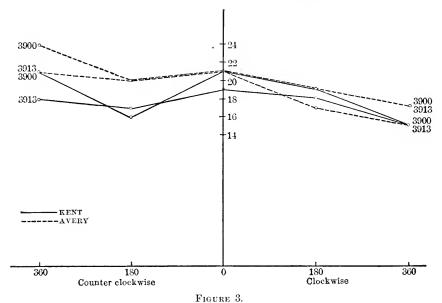
The above facts make it extremely probable that the adjustment of the slit in the previous investigation was good. And, further, if with full length of slit no change in definition could be detected for a rotation of 90°, it is all the more probable that with a slit of 5 mm length, as used in making regular exposures, the definition was the best obtainable.

(2) Further, as to shift as a function of the orientation of the slit, series of plates were taken with the slit oriented approximately 1° and 0.5° of arc clockwise and counter clockwise, including a series at parallelism; or 360° and 180° counter clockwise, 0°, 180°, and 360° clockwise on the divided head. If orientation introduce shift, the shift-orientation curve should either show a point of inflection at zero orientation or cross the displacement axis at that point. Table I, on pages 356 and 357, is self-explanatory. The data given in the table and the curves of Figure III show that for the two lines studied the shift is not influenced by the orientation of the slit.

The values of the shift obtained are, within the limits of error of experiment, the same as those obtained in the previous investigation.

The average deviation from the mean of two measurements (of the shift of a line) on any one plate is 0.003 (Kent) and 0.004 (Avery) t. m. for  $\lambda$  3900.68; and 0.002 (Kent) and 0.003 (Avery) t. m. for  $\lambda$  3913.58. It will be noticed that the value of the shift given on the

#### SHIFT-ORIENTATION CURVE FOR Ti. AA 3900 AND 3913.



Abscissas, Orientation in degrees. Ordinates, Shift in t.m. × 10<sup>3</sup>.

TABLE II.

ARC AND ARC.

|              |          |           | λ 3900               | ).68. |                    | λ 3913.58. |          |                              |        |  |  |  |
|--------------|----------|-----------|----------------------|-------|--------------------|------------|----------|------------------------------|--------|--|--|--|
| Distri       |          |           | Orientation of Slit. |       |                    |            |          |                              |        |  |  |  |
| Plate<br>No. | Date.    | Parallel, | , or 0°.             |       | er clock-<br>360°. | Parallel   | , or 0°. | Counter clock-<br>wise 360°. |        |  |  |  |
|              |          | Kent.     | Avery.               | Kent. | Avery.             | Kent.      | Avery.   | Kent.                        | Avery. |  |  |  |
| 106          | April 27 | -0.001    | 0.003                |       |                    | -0.002     | 0.002    |                              |        |  |  |  |
| 107          | "        | 0.001     | 0.002                |       |                    | 0.004      | 0.003    |                              |        |  |  |  |
| 109          | "        |           |                      | 0.002 | 0.005              |            |          | 0.003                        | 0.002  |  |  |  |

different plates varies considerably. This is probably due to the fact that it was difficult to set the very end of the spark image accurately upon the slit. As shown in the previous paper, the part of the image employed influences the character of the line and the value of the shift.

During the progress of the work it was suggested to us that the use of the tip of the spark line as that part of the line upon which to set the thread of the microscope in measuring was perhaps objectionable owing to the fact that there might be a shift due to diffraction resulting from reducing the virtual aperture of the grating by strips of black paper set only roughly perpendicular to the ruling, the measurement being made by a mm. scale. Three exposures on one plate were therefore made, — all of the arc, and the first and third superimposed as usual. No shift was shown when the slit was either parallel or oriented, as indicated in the table on page 359.

At the end of the series of experiments the water rheostat was cut out of the transformer circuit, and in its place was inserted a choke coil of closed magnetic circuit of U form with adjustable armature. When adjusted roughly to show maximum power as measured by the wattmeter, with a spark-length as indicated in Table III, the shift was increased to 0.032 t. m. in the mean for  $\lambda$  3900.68 and 0.033 t. m. for  $\lambda$  3913.58.

TABLE III.

Conditions same as in Table I, except spark-length = 9 mm, in plate 125 and 15 mm, in plates 126 to 128. Time of exposures for spark = 60 seconds.

|              |          |          |                        |        | λ 390                                 | 0.68.  | λ 3913.58. |        |  |  |
|--------------|----------|----------|------------------------|--------|---------------------------------------|--------|------------|--------|--|--|
| Plate<br>No. | Date.    |          | ons of Pri<br>Circuit. | mary   | Orientation of Slit: Parallel, or 0°. |        |            |        |  |  |
|              |          | Amperes. | Watts.                 | Volts. | Kent.                                 | Avery. | Kent.      | Avery. |  |  |
| 125          | April 27 | 50       | 1000                   | 28     | 0.040                                 | 0.038  | 0.031      | 0.040  |  |  |
| 126          | "        | 49       | 950                    | 27     | 0.033                                 | 0.033  | 0.030      | 0.049  |  |  |
| 127          | "        | 50       | 800                    | 24     | 0.030                                 | 0.030  | 0.032      | 0.029  |  |  |
| 128          | "        | 50       | 800                    | 26     | 0.026                                 | 0.029  | 0.022      | 0.031  |  |  |
|              | Means .  |          |                        |        | 0.032                                 | 0.032  | 0.029      | 0.037  |  |  |

It is the purpose of the author of the former paper to study with an echelon the position of the narrow and less diffuse lines of the titanium spectrum.

In conclusion we wish to acknowledge the kindness shown us by Professor Trowbridge and those associated with him in so generously putting at our disposal all the facilities of the Jefferson Physical Laboratory; and our thanks are due also to the Rumford Committee for the grant made in aid of this research.

DEPARTMENT OF PHYSICS, BOSTON UNIVERSITY. June, 1907.



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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

PRELIMINARY PAPER. - THE ANALYSIS OF LEAD CHLORIDE.

BY GREGORY PAUL BAXTER AND JOHN HUNT WILSON.

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## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

### A REVISION OF THE ATOMIC WEIGHT OF LEAD.

PRELIMINARY PAPER.—THE ANALYSIS OF LEAD CHLORIDE.

BY GREGORY PAUL BAXTER AND JOHN HUNT WILSON.

Presented November 13, 1907. Received October 18, 1907.

Although lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas. Of the earlier determinations of this constant those of Döbereiner and Longchamps can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius, who obtained values ranging from 206.7 to 207.3 by reduction of litharge in a current of hydrogen. Berzelius also synthesized the sulphate from metallic lead with the result 207.0.5 Shortly after, Turner criticized the first method employed by Berzelius and attributed the irregularity of his results to the action of lead oxide on the silicious matter of the tube at the temperature employed in the reduction. By the conversion of both the metal and the oxide into sulphate Turner in a painstaking research deduced the values 207.0

<sup>&</sup>lt;sup>1</sup> Earlier work on the atomic weight of lead has been carefully summarized by Clarke. Smithsonian Miscellaneous Collections, Constants of Nature, "A Recalculation of the Atomic Weights," 1897.

In recalculating the data of earlier determinations the following atomic weights have been used in this paper:

<sup>0=16.000;</sup> Ag=107.88; Cl=35.46; N=14.01; S=32.07 Richards and Wells, Pub. Car. Inst., No. 28 (1905); Richards and Forbes, Ibid., No. 69, p. 47 (1907); Richards and Jones, Ibid., No. 69, p. 69; Report of International Committee on Atomic Weights, Jour. Amer. Chem. Soc., 29, 110 (1907).

<sup>&</sup>lt;sup>2</sup> Schweig. Jour., 17, 241 (1816).

<sup>3</sup> Ann. Chim. Phys., 34, 105 (1827).

<sup>4</sup> Pogg. Ann., 19, 314 (1830).

<sup>&</sup>lt;sup>5</sup> Lehrbuch, 5th ed., 3, 1187 (1845).

<sup>6</sup> Phil. Trans., 527 (1833).

and 207.6 respectively, and by converting the nitrate into sulphate, 204.2. Marignac <sup>7</sup> converted metallic lead into the chloride by heating in a stream of chlorine and obtained the result 207.42. Both Marignac <sup>8</sup> and Dumas <sup>9</sup> analyzed lead chloride. Marignac, who dried the salt at 200°, by iteration against silver found the atomic weight of lead to be 206.81, and from the ratio of lead chloride to silver chloride, 206.85. Dumas subsequently showed that lead chloride, even when dried at 250°, retains moisture and is somewhat basic, and in one analysis in which corrections are applied for these errors, found a somewhat higher value, 207.07, as was to be expected. Chloride analyses by early investigators are, however, to be universally distrusted, owing to neglect of the very considerable solubility of silver chloride, thus producing too low results.

Stas's work upon the syntheses of lead nitrate and sulphate from the metal is undoubtedly the most accurate contribution upon the subject, although a careful consideration of his work discloses minor defects, many of which he recognized himself. The metallic lead used in the syntheses was finally fused under potassium cyanide. Whether or not this treatment introduced impurities into the metal is uncertain. Stas himself suspected the presence of alkalies in the metal. Since the nitrate could not be dried above 150° without decomposition, it undoubtedly contained moisture, and Stas calls attention to this point. The sulphate was made by treatment of lead nitrate, resulting from the nitrate syntheses, with sulphuric acid. The sulphate was dried finally at dull redness, and was probably free, or nearly free, from moisture, although it may have contained traces of lead oxide resulting from occluded nitrate, as well as sulphuric acid. Most of these probable errors tend to lower the observed atomic weight, so that Stas's value from the series of nitrate syntheses, 206.81, and that from the sulphate series, 206.92, are to be regarded as minimum values. The reader of Stas's own account of his work upon lead cannot fail to be impressed with the fact that he was somewhat dissatisfied with the outcome of his research. Mention should also be made of the work of Anderson and Svanberg 11 on the conversion of lead nitrate into oxide, although the method was primarily employed in an endeavor to fix the atomic weight of nitrogen. Their results yield the value 207.37.

The discrepancies between the results of these various experiments

<sup>7</sup> Lieb. Ann., 59, 289 (1846).

<sup>&</sup>lt;sup>8</sup> Jour. Prakt. Chem., 74, 218 (1858).

<sup>&</sup>lt;sup>9</sup> Lieb. Ann., **113**, 35 (1860).

<sup>10 (</sup>Euvres Completes, 1, 383.

<sup>&</sup>lt;sup>11</sup> Ann. Chim. Phys. (3), 9, 254 (1843).

only serve to emphasize the need of a redetermination of the value in question, and it was with this object in view that the work embodied in this paper was undertaken.

The search for a suitable method for determining the atomic weight of lead failed to reveal any more promising line of attack than those already employed for the purpose. With an element of so high an atomic weight as lead, in any method involving the change of one of its compounds into another, errors which may be insignificant with elements of small atomic weight are magnified in the calculations to undesirable proportions. Furthermore, during the following investigation, reduction of the chloride and oxide in hydrogen was investigated far enough to show that complete reduction of either compound was extremely difficult, if not impossible, without loss of material from the containing vessel by sublimation, aside from the fact that all available material for containing vessels is acted upon by either the fused salt or the reduced metal. The elimination of moisture from lead nitrate or lead sulphate without decomposition of the salts seemed likely to prove a stumbling block in the use of these substances. Finally, in spite of the slight solubility of lead chloride, the determination of the chlorine in this salt by precipitation with silver nitrate was chosen as presenting fewest difficulties. In the first place, the determination of a halogen can be effected with great accuracy. In the second place, the elimination of moisture from lead chloride is an easy matter, since the salt may be fused in a platinum vessel in a current of hydrochloric acid gas without attacking the platinum in the least and without the production of basic salts. In the third place, silver chloride, which has been precipitated from a dilute solution of lead chloride by means of silver nitrate, does not contain an amount of occluded lead salt large enough to be detected.

#### Purification of Materials.

Water. — All of the water used in either the purification or the analyses was distilled twice, once from an alkaline permanganate solution and once from very dilute sulphuric acid. Block tin condensers were used in both distillations, and rubber and cork connections were avoided. Generally receivers of Jena glass were employed, but in certain cases the water was collected in platinum or quartz vessels.

Hydrochloric acid. — Commercial C. P. hydrochloric acid was diluted with an equal volume of water and distilled with a quartz condenser, only the middle fraction being collected.

Nitric acid. — Nitric acid was distilled with a platinum condenser,

until free from chlorine. Two distillations were invariably sufficient to accomplish this end, if the first third of each distillate was rejected.

Silver. - Pure silver was obtained by methods already many times employed in this laboratory. Silver nitrate was dissolved in a large volume of water and the silver was precipitated as chloride with an excess of hydrochloric acid. The precipitate was thoroughly washed and reduced with alkaline invert sugar. The reduced silver, after being washed, was dried and fused on charcoal in the flame of a clean blast lamp. After the buttons had been cleaned by scrubbing with sand and etching with nitric acid, they were dissolved in pure dilute nitric acid and the silver was precipitated as metal with ammonium formate. 12 This silver was washed and fused in the flame of a blast lamp on a crucible of the purest lime. The buttons were cleaned as before, and then electrolyzed. 13 Finally the electrolytic crystals were fused in a boat of the purest lime in a porcelain tube in a current of pure electrolytic hydrogen. 14 The bars of silver were cut in pieces with a fine steel saw, etched with dilute nitric acid until free from iron, washed, dried, and heated in a vacuum to 400°C. The silver was kept in a desiccator containing solid potassium hydroxide.

Lead chloride. — Three samples of lead chloride from two entirely different sources were employed. Sample A was prepared from metallic lead. Commercial lead was dissolved in dilute nitric acid, and the solution, after filtration, was precipitated with a slight excess of sulphuric acid. The lead sulphate was thoroughly washed, suspended in water, and hydrogen sulphide was passed in until the sulphate was almost completely converted into sulphide. Next the sulphide was washed with water, dissolved in hot dilute nitric acid, and the solution was freed from sulphur and unchanged sulphate by filtration. lead nitrate thus obtained was crystallized twice, dissolved in water, and precipitated in class vessels with a slight excess of hydrochloric acid. The chloride was washed several times with cold water and then crystallized from hot water eight times, the last five crystallizations being carried out wholly in platinum, with centrifugal drainage after each crystallization. In crystallizing the lead chloride the whole sample was not dissolved at one time, but the same mother liquor was used for dissolving several portions of the original salt. Needless to say, the chloride was not exposed to contact with the products of combustion of illuminating gas, lest lead sulphate be formed.

Sample B was prepared from commercial lead nitrate. This salt was

<sup>&</sup>lt;sup>12</sup> Richards and Wells, Pub. Car. Inst., No. 28, 19 (1905).

<sup>13</sup> Abrahall, Jour. Chem. Soc. Proc., 1892, p. 660.

<sup>&</sup>lt;sup>14</sup> Baxter, These Proceedings, 39, 249 (1903).

dissolved and crystallized from dilute nitric acid once in glass and six times in platinum vessels, with centrifugal drainage. Hydrochloric acid was then distilled into a large quartz dish, and the solution of the nitrate was slowly added with constant stirring with a quartz rod. The chloride was freed from aqua regia as far as possible by washing with cold water, and was once crystallized from aqueous solution in quartz dishes to remove last traces of aqua regia. Finally the salt was crystallized three times in platinum.

It could reasonably be expected that both of these samples were of a high degree of purity; nevertheless, upon heating the salt in an atmosphere of hydrochloric acid, the salt itself turned somewhat dark, and upon solution of the fused salt in water a slight dark residue remained. Although in a few preliminary experiments attempts were made to determine this residue by filtration and ignition, it was subsequently found that even a small filter paper adsorbs appreciable amounts of lead compounds from a solution of the chloride, which cannot be removed by washing with water. From three to thirteen hundredths of a milligram of residue were obtained in several blank experiments, by ignition of filters through which half per cent solutions of lead chloride had been passed, with subsequent very thorough washing. In order to avoid the uncertainty of this correction, further attempts were made to obtain a sample of the salt which would give a perfectly clear solution in water after fusion, and thus render filtration unnecessary. With this end in view a considerable quantity of Sample A was fused in a large platinum boat in a current of hydrochloric acid. The fused salt was powdered in an agate mortar, dissolved in water in a platinum vessel, and the solution was freed from the residue by filtration through a tiny filter in a platinum funnel into a platinum dish, where it was allowed to crystallize. This sample was then twice recrystallized with centrifugal drainage. Notwithstanding the drastic treatment to which it had been subjected, when a portion of this material was fused in hydrochloric acid, the same darkening as before was observed, and the same residue was obtained. The suspicion that the difficulty was due to dissolving of the filter paper by the solution of the salt 15 led to a second more successful attempt by crystallization from hydrochloric acid solution in platinum vessels. In this way it was found possible to prepare salt which showed no tendency to darken upon heating, and which, after fusion, left absolutely no residue upon solution in water. Portions of Samples A and B were thus recrystallized three times Since these two specimens of material gave identical results,

<sup>15</sup> Mr. P. B. Goode in this laboratory has recently found a similar difficulty with the chlorides of the alkaline earths.

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for two final experiments, portions from each of these samples were mixed and then subjected to three additional crystallizations. This last sample was designated Sample C.

### METHOD OF ANALYSIS.

The lead chloride contained in a weighed platinum boat was first fused in a current of pure dry hydrochloric acid gas. This gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and after being washed with a saturated solution of hydrochloric acid, was passed through five towers filled with beads moistened with freshly boiled concentrated sulphuric acid, to dry the gas. It has already been shown that phosphorus pentoxide may not be used for this purpose. 16 After the salt had cooled, the hydrochloric acid was displaced by dry nitrogen, and this in turn by dry air. Nitrogen was prepared by passing air charged with ammonia over redhot rolls of copper gauze, the excess of ammonia being removed by means of dilute sulphuric acid. The gas was passed over beads moistened with a dilute silver nitrate solution and over solid caustic potash to remove sulphur compounds and carbon dioxide respectively, and was finally dried by concentrated sulphuric acid and phosphorus pentoxide. The air was purified and dried in a similar fashion. The apparatus for generating the hydrochloric acid and for purifying the hydrochloric acid and nitrogen was constructed wholly of glass with ground-glass The platinum boat containing the fused chloride was next transferred to a weighing bottle without exposure to moist air, by means of the bottling apparatus, which has frequently served for a similar purpose in many atomic weight investigations in this laboratory. 17 After standing some time in a desiccator in the balance room, the weighing bottle was weighed. In most of the analyses the lead chloride was dissolved from the boat by prolonged contact with boiling water in a Jena glass flask. In the last two analyses, in order to show that no error was introduced through solubility of the glass, the solution was prepared in a large platinum retort, and was not transferred to the precipitating flask until cold.

Very nearly the necessary amount of pure silver was then weighed out and dissolved in redistilled nitric acid diluted with an equal volume of water in a flask provided with a column of bulbs to prevent loss by spattering. After the silver was all dissolved, an equal volume of water was added, and the nitrous fumes were expelled

<sup>&</sup>lt;sup>16</sup> Baxter and Hines, Jour. Amer. Chem. Soc., 28, 779 (1906).

<sup>17</sup> Richards and Parker, These Proceedings, 32, 59 (1896).

by gentle heating. The solution was then further diluted until not stronger than one per cent, and added slowly, with constant agitation, to the solution of lead chloride contained in the precipitating flask. The precipitation and handling of the silver chloride were conducted in a room lighted with ruby light. shaken for some time and allowed to stand for a few days, with occasional agitation, until the supernatant liquid had become clear. Thirty cubic centimeter portions of the solution were then removed and tested with hundredth normal silver nitrate and sodium chloride. in a nephelometer, 18 for excess of either chloride or silver, and, if necessary, standard silver nitrate or sodium chloride was added, and the process of shaking and testing repeated until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask, since they contained appreciable amounts of silver chloride, and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced. Furthermore, if an excess of silver was found, a negative correction of an equivalent quantity of silver chloride was necessary.

After the exact end point had been obtained, about two tenths of a gram of silver nitrate in excess was added in order to precipitate the dissolved silver chloride, and the flask was thoroughly shaken, and allowed to stand again until the solution was perfectly clear. silver chloride was washed, first several times with a very dilute silver nitrate solution containing four hundredths of a gram per litre, and then eight times with pure water. It was next transferred to a Gooch crucible and dried for several hours in an electric oven, the temperature being gradually raised to 180°, and was cooled in a desiccator and weighed. In every case the moisture retained by the precipitate was determined by fusion in a small porcelain crucible. The silver chloride, dissolved in the filtrate and washing, was determined by comparison with standard solutions in the nephelometer in the usual manner. Care was taken to treat both tubes in exactly the same manner, and final readings were taken only when the ratio had become constant. Before proceeding to the nephelometer tests, however, the filtrate and washings were passed through a very small filter in order to collect a small quantity of asbestos shreds mechanically detached from the Gooch crucible. The filter was ignited and weighed, the ash being treated with a drop of nitric and hydrochloric acid in order to convert any reduced silver into chloride. In order to find out whether lead or silver nitrates were appreciably adsorbed by the filter paper, a solution

<sup>&</sup>lt;sup>18</sup> Richards and Wells, Am. Ch. J., 31, 235 (1904); 35, 510 (1906).

### THE ATOMIC WEIGHT OF LEAD.

Series I.  $PbCl_2: 2 Ag$ .

Ag = 107.930 Cl = 35.473

| Number<br>of<br>Analysis. | Sample<br>of<br>PbCl <sub>2</sub> . | Weight of<br>PbCl <sub>2</sub><br>in Vacuum. | Weight of<br>Ag in<br>Vacuum. | Weight of Ag added or subtracted. | Corrected<br>Weight<br>of Ag. | Atomic<br>Weight of<br>Pb. |
|---------------------------|-------------------------------------|----------------------------------------------|-------------------------------|-----------------------------------|-------------------------------|----------------------------|
|                           |                                     | grams                                        | grams                         | gram                              | grams                         |                            |
| 1                         | A                                   | 4.67691                                      | 3.63061                       | -0.00074                          | 3.62987                       | 207.179                    |
| 2                         | A                                   | 3.67705                                      | 2.85375                       | 0.00000                           | 2.85375                       | 207.189                    |
| 3                         | Λ                                   | 4.14110                                      | 3.21388                       | +0.00020                          | 3.21408                       | 207.173                    |
| 4                         | Λ                                   | 4.56988                                      | 3.54672                       | 0.00000                           | 3.54672                       | 207.185                    |
| 5                         | В                                   | 5.12287                                      | 3.97596                       | -0.00028                          | 3.97568                       | 207.201                    |
| 6                         | В                                   | 3.85844                                      | 2.99456                       | 0.00000                           | 2.99456                       | 207.186                    |
| 7                         | В                                   | 4.67244                                      | 3.62628                       | 0.00000                           | 3.62628                       | 207.189                    |
| 8                         | С                                   | 3.10317                                      | 2.40837                       | 0.00000                           | 2.40837                       | 207.188                    |
| 9                         | С                                   | 4.29613                                      | 3.33427                       | -0.00020                          | 3.33407                       | 207.202                    |
| Averag                    | Average                             |                                              |                               |                                   |                               |                            |

## Series II. PbCl<sub>2</sub>: 2 AgCl.

| Number<br>of<br>Analysis.                                             | Sample<br>of<br>PbCl <sub>2</sub> . | Weight of<br>PbCl <sub>2</sub> in<br>Vacuum, | Weight of<br>AgCl in<br>Vacuum. | Loss<br>on<br>Fusion. | Weight<br>of<br>Asbestos. | Wt. AgCl<br>from<br>Wash<br>Waters. | Corrected<br>Weight<br>of AgCl. | Atomic<br>Weight<br>of Pb. |
|-----------------------------------------------------------------------|-------------------------------------|----------------------------------------------|---------------------------------|-----------------------|---------------------------|-------------------------------------|---------------------------------|----------------------------|
| 10                                                                    | Λ                                   | grams<br>4.67691                             | grams<br>4.82148                | gram<br>0.00100       | gram<br>0.00021           | gram<br>0.00204                     | grams<br>4.82273                | 207.188                    |
| 11                                                                    | Λ                                   | 4 14110                                      | 4 26848                         | 0.00020               | 0.00008                   | 0.00180                             | 4.27016                         | 207.192                    |
| 12                                                                    | В                                   | 5.12287                                      | 5.28116                         | 0.00054               | 0.00013                   | 0.00197                             | 5.28272                         | 207.181                    |
| 13                                                                    | В                                   | 3.85844                                      | 3.97759                         | 0.00035               | 0.00033                   | 0.00192                             | 3.97949                         | 207.136                    |
| 14                                                                    | С                                   | 3.10317                                      | 3.19751                         | 0.00045               | 0 00014                   | 0.00189                             | 3.19909                         | 207.261                    |
| 15                                                                    | С                                   | 4.29613                                      | 4.42730                         | 0.00020               | 0.00004                   | 0.00268                             | 4 42982                         | 207.204                    |
| Average, rejecting the least satisfactory analyses, 13 and 14 207.191 |                                     |                                              |                                 |                       |                           | 207.193<br>207.191<br>207.190       |                                 |                            |

containing lead nitrate, silver nitrate, and nitric acid of the concentration of these filtrates, was passed through several small filter papers, which were then very carefully washed. In four cases, after incineration of the papers, there was found, —0.00001, +0.00002, +0.00003, +0.00001 gram of residue, exclusive of ash. This correction is so small that it is neglected in the calculations. In all the analyses the platinum boat behaved admirably, the loss in weight never amounting to more than a few hundredths of a milligram.

The balance used was a short arm Troemner, easily sensitive to a fiftieth of a milligram. The gold-plated brass weights were carefully standardized to hundredths of a milligram. All the weighings were made by substitution with tare vessels as nearly like those to be weighed as possible.

Vacuum corrections: The values of the density of lead chloride as given by various observers range from 5.78 to 5.805, <sup>19</sup> the mean of the more accurate determinations being 5.80. This gives rise to a vacuum correction of +0.000062 for each apparent gram of lead chloride, the density of the weights being assumed to be 8.3. The other vacuum corrections applied were silver chloride, +0.000071, and silver, -0.000031.

All analyses which were carried to a successful completion are recorded in the preceding tables.

The close agreement of the averages of the two series is strong evidence that no constant error, such as occlusion, affects the results. Furthermore, in all, 19.55663 grams of silver produced 25.98401 grams of silver chloride, whence the ratio of silver to silver chloride is 132.865, a value in close agreement with the result 132.867 obtained by Richards and Wells.<sup>20</sup> Furthermore, the different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107.93 (0 = 16.000), the atomic weight of lead is 207.19, nearly three tenths of a unit higher than the value now in use. If the atomic weight of silver is 107.88, a value probably nearer the truth than 107.93, lead becomes 207.09, a number still much higher than that depending upon Stas's syntheses, as is to be expected.

We are greatly indebted to the Carnegie Institution of Washington for assistance in pursuing this investigation, also to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

Cambridge, Mass., October 18, 1907.

<sup>19</sup> Landolt-Börnstein-Meyerhoffer, Tabellen.



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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

A SIMPLE METHOD OF MEASURING THE INTENSITY OF SOUND.

BY GEORGE W. PIERCE.



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#### I. Introduction.

In the course of a series of experiments on Detectors for Electromagnetic waves the writer has found a number of solid substances which, when supplied with contact electrodes and put into electric circuits, serve as rectifiers for small electric oscillations. Some of these substances used in connection with a galvanometer prove to be extremely sensitive and constant in their action and permit the measurement of the currents generated by the vibration of the diaphragm of a magneto-telephone under the action of sound waves even when the telephone is at a considerable distance from the source of sound.

With the use of this device the relative intensity of sound at different positions in a room may be measured, and many interesting results as to the acoustic properties of an auditorium may be obtained.

The study of the rectifiers themselves is the subject of a series of papers by the writer, on "Crystal Rectifiers for Electric Currents and Electric Oscillations." Part I of this series of papers appeared in the Physical Review for July, 1907, Vol. XXV, pp. 31–60. The rectifier there investigated is Carborundum. Several other crystal bodies, some of which are in their action much more sensitive than carborundum, possess similar properties and are being experimentally studied in detail with reference to their electrical characteristics and with reference to their use in electric-wave telegraphy.

The results of this study will constitute the subject matter of succeeding parts of the Physical Review article.

### II. MOLYBDENITE AS A RECTIFIER FOR ELECTRIC OSCILLATIONS.

One of the most sensitive of the rectifiers thus far investigated is Molybdenite. The present paper deals with the use of the molybdenite rectifier in the measurement of sound.

Molybdenite is also an extremely sensitive detector for electric waves in wireless telegraphy, and may also be employed in experiments on telephony and in many other experiments where it is required to measure small electric oscillations.

The manner of mounting and employing the substance is substantially the same in these several applications, and is capable of several variations, only one of which will be given here. Molybdenite, MoS<sub>2</sub>, is a mineral occurring in nature in the form of hexagonal prisms with eminent cleavage parallel to the base, and may be scaled off in thin sheets, a few sq. cm. in area, resembling bits of tin-foil. In the present experiments a thin sheet so obtained was mounted in the manner shown in the sectional drawing of Figure 1.

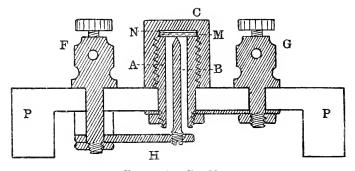


FIGURE 1. - Rectifier.

A thin, circular piece of molybdenite <sup>1</sup> (M, Figure 1), about 1 sq. cm. in area, is clamped tightly between a piece of mica N and the hollow brass post A, by means of a brass cap C screwed down on the post A. The molybdenite is thus held in electrical connection with the annular surface of the end of the hollow brass post A, which is in turn metallically connected with the binding post G. Separated from A by an air space, a small pointed brass rod B is screwed up through a metallic strip H attached to a second binding post F. The binding posts and the holder for the molybdenite are rigidly supported by a porcelain base PP. The seat of the action of the molybdenite as a rectifier is at the small region of contact between the molybdenite and the pointed rod. In the construction of the rectifier this contact is adjusted by screwing the rod up through H until a galvanometer in series with the device and a source of alternating voltage (of about .05 volt) gives

<sup>&</sup>lt;sup>1</sup> Molybdenite free from iron should be used.

a maximum deflection. The adjustment of the contact is made once for all, and subsequent accidental changes of the apparatus is prevented by filling the cavity about H with melted wax or plaster of Paris.

When made in this manner the rectifier will stand considerable abuse in the way of jar and overload. It is, however, subject to changes due to the expansion and contraction of the mounting, and due also possibly to a temperature coefficient of the molybdenite itself. Effort to get a mounting without such changes with temperature and a study of the temperature coefficient of the substance itself are now in progress. Up to the present it is found advisable to use the rectifier in a thermostat at constant temperature, when accurate quantitative agreement between observations extending over a considerable period of time is required.

Whether or not the direct current obtained from the molybdenite in contact with two unequal electrodes is a thermo-electric action due to the unequal heating of the electrodes by the oscillating current is at present not known. It will be seen that the conditions are favorable for such thermo-electric action. In order not to commit one's self to any particular theory as to the nature of the action, the device is here referred to as a "rectifier," in that the current in one direction due to an impressed voltage is very different from the current in the opposite direction under the same voltage.

## III. ELECTRIC CIRCUITS EMPLOYED WITH THE MOLYBDENITE RECTIFIER IN EXPERIMENTS ON SOUND.

In the measurement of sound, the rectifier was at first placed directly in series with a sensitive galvanometer and a Bell magneto-telephone receiver. With this arrangement, when sound was made in the neighborhood of the receiver, the vibration of the telephone diaphragm generated electric oscillations in the circuit. These oscillations passed through the rectifier more strongly in one direction than in the opposite direction, and caused a deflection of the galvanometer.

However, on account of the high resistance of the rectifier, and in order to take advantage of electrical resonance in the circuits, it was found better to employ an arrangement of circuits containing a step-up transformer, as is shown in Figure 2.

In Figure 2 PS is a transformer, the primary P of which is connected in series with the telephone T and an adjustable condenser C. The secondary S of the transformer is connected in series with the rectifier R, the galvanometer G, and a calibrating device at W. By adjusting the condenser C, the electric circuit TCP was brought to

resonance with the alternating voltage impressed on the system by the periodic impact of the sound waves. This adjustment was easily made experimentally.

The proper choice of the transformer PS and the telephone T was a more difficult problem. A theoretical solution of this problem was not at hand, on account of lack of knowledge of the characteristics of the telephone when used as a generator of oscillatory currents and on account of the fact that the current through the crystal in the secondary is not a simple function of the voltage in this circuit (see Figure 6). Some aid in the choice was had in the following considerations, which served to point vaguely the direction in which experiment was to be made:

1. Since the primary circuit was to be brought to resonance with the oscillations, the inductance of the primary circuit is negligible, if we

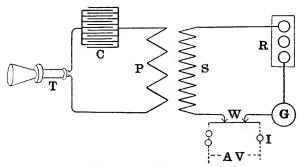


Figure 2. - Electric circuit.

may neglect the reaction of the secondary circuit on the primary. With this approximation it follows from elementary considerations that the resistance of the primary coil should be equal to the resistance of the telephone. Experiment soon showed that the reaction of the secondary circuit was not negligible, and since the effect of the reaction of the secondary is to increase the apparent resistance of the primary, it follows that the resistance of the primary coil should be somewhat less than that of the telephone.

2. The iron core of the transformer should be such as to be properly magnetizable by the current generated by the telephone, which in frequency and intensity approaches to the current used in telephony. Whence it seemed probable that the small terminal transformers used in telephony would have about the proper amount of iron for use in the present experiments.

3. The resistance of the secondary of the transformer and that of the galvanometer should be high because the resistance of the crystal for a small current is several thousand ohms.

Guided by these considerations, and by the results of preliminary experiments with several small induction coils, two transformers were wound, of which the one that proved the more satisfactory had the following dimensions:

Length of iron core, 9.5 cm. Diameter of iron core, 1 cm. Depth of channel, 1.5 cm.

In this channel were three coils of which either pair could be used as primary and secondary. These three coils had respectively 16, 280, and 720 ohms resistance.

With this transformer experiments were made with three different telephones, of which a Siemens and Halske "Lautsprecher," rewound to 466 ohms, and provided with a small conical sound collector 10 cm. in diameter, proved the most sensitive. This telephone was ordinarily used with the 280 ohm primary and the 720 ohm secondary. The other two telephones used had resistances of 53.8 and 99.8 ohms respectively, and were used with the 16 ohm primary and the 720 ohm secondary.

Experiment I. Adjustment of the Receiving Telephone Circuit to Resonance with the Sound. — After having made a preliminary selection of the pitch to be employed in a particular experiment, it becomes important to adjust the electrical circuit to resonance with this pitch. The following data is given to show the manner in which this adjustment is made, and to show the effect of such a resonant adjustment in increasing the sensitiveness of the apparatus.

An organ-pipe F\$\pmu\_4\$ giving 705 complete vibrations per second, supplied by air from bellows operated by an electric blower and set up in the Constant Temperature Room 2 of the Jefferson Physical Laboratory, served as source of the sound.

The telephone receiver, having a resistance of 53.8 ohms, and pro-

<sup>&</sup>lt;sup>2</sup> This room is described in Professor Sabine's paper on "Architectural Acoustics, Part I, Reverberation," published in the American Architect, Vol. XLVIII, April-June, 1900, and in Contributions from the Jefferson Physical Laboratory, Vol. IV, 1906. This room was used in some of the present experiments because the apparatus for producing the sound happened to be in place there. The apparatus was in use by Professor Sabine, and together with other parts of the apparatus, including two of the receiving telephones, was kindly placed by him at my disposal.

vided with a conical sound-collector 29 cm. in diameter, was placed at a distance of about 1.5 meters from the organ-pipe. The 16 ohm primary and the 720 ohm secondary of the transformer, Figure 2, were employed. The galvanometer G was a d'Arsonval type and had a resistance of 538 ohms, and gave a throw of one scale division ( $\frac{1}{10}$  inch) for a current of  $1.53 \times 10^{-8}$  amperes.

The condenser C, Figure 2, having a total capacity of 1 microfarad, and adjustable by steps of .05 microfarads, was given various values, and the corresponding throws of the galvanometer when the pipe was sounded were taken. In taking these readings the pipe was left sounding until the coil of the galvanometer had completed its swing.

The results are recorded in Table I.

TABLE I.

Adjustment of Electric Circuit to Resonance with Sound Frequency.

| Capacity of C in Microfarads. | Current through Galva-<br>nometer in Microamperes. |  |  |  |  |
|-------------------------------|----------------------------------------------------|--|--|--|--|
| .00                           | .000                                               |  |  |  |  |
| .20                           | .064                                               |  |  |  |  |
| .30                           | .308                                               |  |  |  |  |
| .45                           | .477                                               |  |  |  |  |
| .50                           | .470                                               |  |  |  |  |
| .60                           | .320                                               |  |  |  |  |
| .80                           | .206                                               |  |  |  |  |
| 1.00                          | .157                                               |  |  |  |  |
| C short-circuited             | .061                                               |  |  |  |  |

The curve of Figure 3 is plotted from the data of Table I. The horizontal dotted line through the figure is the current with the condenser short-circuited. This curve gives an idea of the advantage obtained by the use of the proper capacity in the primary circuit of Figure 2. The maximum of the curve shows a value of the current that is nearly eight times the current obtained when the condenser was short-circuited.

### IV. STATIONARY SOUND WAVES. DISTRIBUTION OF INTENSITY.

In taking the data of Experiment I, the position of the telephone receiver and that of the organ-pipe were left constant. When the telephone was removed to different parts of the room, very striking evidence

of a stationary-wave system was obtained. This stationary system was, however, extremely complicated. some positions, for example, a very slight change of the inclination of the sound-collecting cone, without any motion of the receiver as a whole toward or away from the source of sound, would cause several hundred per cent change of the reading of the galvanometer. Professor Sabine has already called attention to the existence in this room of a striking interference system. The following paragraph descriptive of

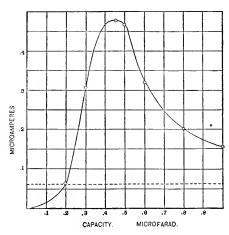


FIGURE 3. - Resonance curve.

the phenomenon is quoted from his writings on the subject:

"This room is here described at length because it will be frequently referred to, particularly in this matter of interference of sound. While working in this room with a treble c gemshorn organ-pipe blown by a steady wind pressure, it was observed that the pitch of the pipe apparently changed an octave when the observer straightened up in his chair from a position in which he was leaning forward. The explanation is this: The organ-pipe did not give a single pure note, but gave a fundamental treble c accompanied by several overtones, of which the strongest was in this case the octave above. Each note in the whole complex sound had its own interference system, which, as long as the sound remained constant, remained fixed in position. It so happened that at these two points the region of silence for one note coincided with the region of reinforcement for the other, and vice versa. Thus the observer in one position heard the fundamental note, and in the other. The change was exceedingly striking, and as the the first overtone. note remained constant, the experiment could be tried again and again. With a little search it was possible to find other points in the

room at which the same phenomenon appeared, but generally in less perfection." <sup>3</sup>

Before undertaking the study of the complicated distribution of sound intensity in a room with highly reflective walls, it was decided to become better acquainted with the present experimental method by an examination of a much simpler interference system; namely, that produced as nearly as may be by a single reflecting surface. This is done in Experiment II following. Afterward, in Experiment III, it is shown to be practicable to extend the investigation to a quantitative determination of the distribution in a large auditorium.

Experiment II. Stationary Wave Produced by a Single Reflecting Surface.—The arrangement of apparatus is shown in Figure 4. In order to reduce the effects of reflection from the walls of the room,

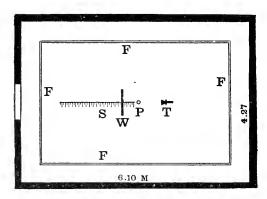


Figure 4. - Position of apparatus in constant temperature room.

they were curtained off with felt, F, 1.1 cm. thick, hung at a distance of about 50 cm. from the walls. Felt of the same thickness was also placed overhead, separated from the ceiling by about 50 cm.

The organ-pipe, F\$\psi\_4\$, 705, serving as a source of sound, was placed at P, near the center of the room. The telephone receiver, used in Experiment I, was placed at T, about 70 cm. from the pipe. Leads ran from the telephone to the condenser and transformer, which together with the observer and galvanometer were in a distant room.

A reflecting surface of wood, 73 cm. wide by 122 cm. high, was placed vertically at W, and was mounted on a track so as to be capable of dis-

<sup>&</sup>lt;sup>3</sup> Sabine, loc. cit. p. 8.

placement along the scale S. The open end of the pipe was placed at a height of 61 cm., and was therefore on a level with the middle of the reflector.

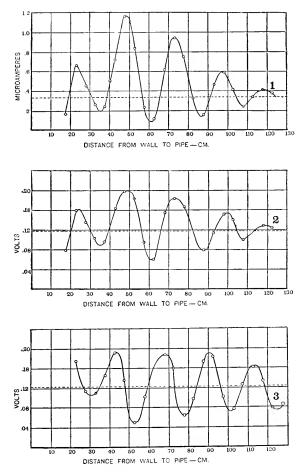


FIGURE 5.—Curve 1, stationary wave in terms of current in secondary. Curves 2 and 3, stationary waves in terms of voltage in secondary.

The distance from the reflector W to the pipe P could be varied and was read off on the scale S. Readings of the galvanometer were taken with the reflector at various stages, 5 cm. apart, along the scale. The values of the current in the galvanometer circuit are plotted against

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the distance of the reflector from the pipe, in Curve 1 of Figure 5. This curve shows the stationary wave system set up by the interference of the direct and the reflected waves. The distances between alternate nodes and alternate loops of the curve give the following values of the wave-length:

The velocity of sound at the temperature of the room, 18°, was 34200 cm. per second, whence the period

$$n = \frac{34200}{48.4} = 706,$$

while the actual value of the pitch of the pipe F<sup>2</sup> 4 is 705 vibrations per second. This agreement is evidently better than is to be expected from the method, on account of the uncertainty of locating the nodes and loops of the curve.

It is seen, however, that the points of the stationary wave lie well on the curve. A repetition of the observation on a succeeding day gave substantial agreement with Curve 1. It is to be observed that the first maximum, with the reflector in the neighborhood of 23.5 cm. from the pipe, is weaker than the second and third maxima. This is probably caused by the fact that the wind-chest on which the pipe was mounted intercepted the reflected wave more strongly when the reflector was close up than when it was more distant from the pipe.

The horizontal dotted line through the curve at 3.30 gives the magnitude of the current when the reflector was removed. It is seen that the peaks of the curve above the line of no reflector are much greater than the neighboring depressions of the curve below the line. This distortion was found to be chiefly due to the current-voltage characteristic of the rectifier, and is eliminated by the calibration of the rectifier with an alternating voltage, and by plotting the stationary wave in terms of alternating voltage instead of galvanometer current.

In making the substitution of voltage for current it would be instructive to impress the known alternating voltage on the primary of Figure 2, and take the corresponding throws of the galvanometer in the secondary. We should then be able to know the voltage generated by the telephone when we know the galvanometer current. However, on account of the influence of the transformer, this could be properly done only with an alternating voltage of the same frequency as the sound, in this case 705 cycles. A generator for this frequency was not

at the writer's disposal, so it was decided to calibrate the secondary circuit instead of the primary. For this, a 60 cycle alternating voltage could be employed without much error; for a preliminary experiment had shown that the impedance of the secondary of the transformer was practically negligible in comparison with the resistance of the rectifier, and that the current-voltage characteristic of the rectifier, as far as tests could be made with means at hand, was independent of the frequency.

The calibration of the secondary circuit was made as follows: The slide wire of a potentiometer was inserted at W in Figure 2, and a source of alternating voltage was applied at AV. The drop of potential in W

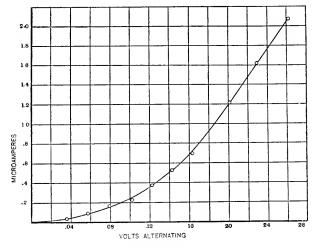


FIGURE 6. - Current-voltage characteristic of rectifier.

was known from the resistance of W and the readings of an alternating current ammeter at I. The alternating voltage in W was varied by varying the resistance of W, and the corresponding direct current in the galvanometer was read. These values are plotted in Figure 6.

If now we replace the current values in Figure 5 by the corresponding voltage values in the secondary of the transformer we obtain Curve 2 of Figure 5. This curve is independent of the rectifier, and shows the number of alternating volts at the terminals of the secondary of the transformer of Figure 2 for various positions of the reflecting wall in Figure 4. Except for distortion of the wave when the reflector was too close to the pipe this curve is nearly symmetrical about the line of no reflector.

Curve 3 of Figure 5 is another curve obtained in the same way with a slate reflector at W and a pipe of slightly higher pitch, and with the Siemens and Halske telephone, which had a much smaller sound collecting cone, 10 cm. in diameter. This curve is somewhat more nearly symmetrical in character.

It should be noted in respect to these curves that there was still considerable reflection from the room, in spite of the felt curtains, and that these reflected waves act in a manner to distort the stationary system.

The curves of Figure 5, although taken under somewhat artificial conditions are in themselves instructive, in showing the marked effect of a reflecting wall on the loudness and quality of sounds. When a speaker or an orchestra is at any given distance in front of a reflecting wall certain tones will be greatly reduced in intensity while tones of a different pitch will be greatly intensified, thus it may be changing completely the emphasis and quality of the composition. When there is only a single strongly reflecting wall (the other walls being strongly absorbtive) this distortion occurs over practically the whole room, although, of course, at different points in the room different notes will be suppressed or emphasized depending on the phase difference between the direct and reflected waves to the auditor.

Experiment III. Interference of Sound Waves in a Large Lecture Room. — In order to extend the investigation to the study of the distribution of sound intensity in a room of considerable proportions, an organ-pipe and the telephone receiver were set up in the large lecture room of the Jefferson Physical Laboratory. This room, of which a diagram is shown in Figure 7, is 18.6 meters long, 12.7 meters wide, and 7.7 meters high at one end. It contains seats for about 300 students. These seats are progressively raised toward the back of the room so that the height of the ceiling above the seats in the rear is about 4 meters. The walls of the room are of brick.

The organ-pipe used as a source of sound, G<sub>4</sub>. 768, was placed at the position P in the diagram, and was supplied with wind at a constant pressure from a reservoir, from which the air supply to the pipe was turned on and off by an electro-pneumatic valve operated by a battery and clock work.

The Siemens and Halske telephone receiver, 466 ohms, with the sound-collecting cone 10 cm. in diameter, was used as a receiver for the sound and was provided with a long double lead so that it could be placed anywhere in the room.

The first position chosen for the receiver was at the extreme rear of

the room (1, Figure 7), where a small track 10 cm. wide and 2 meters long was run out perpendicularly from the wall. The telephone was placed on this track with the opening of the sound collector toward the wall, and readings of the galvanometer were taken with the telephone at various distances from the wall. The results obtained are plotted in Curve 4 of Figure 8. The abscissae of this curve are the distances in centimeters from the wall measured to the opening of the sound col-

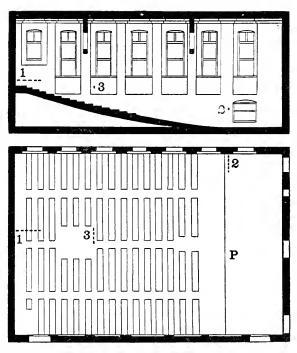


Figure 7.—Diagram of large lecture room. P is the position of the source of sound; 1, 2, and 3, positions of the receiver.

lector; the ordinates are the corresponding values of the current obtained in the galvanometer when the organ-pipe was sounded. The first reading,  $.73 \times 10^{-7}$  amperes, was obtained with the opening of the sound collector of the telephone jammed tight against the brick wall. On withdrawing the receiver from the wall by stages of 5 cm., while keeping the opening of the sound collector always toward the wall, the succeeding values of the curve were obtained, showing the occurrence in this part of the room of very decided maxima and minima of

sound intensity. The irregularities of the curve were actually existent in the interference system and were verified by a repetition of the experiment.

In the above curve the current obtained at the best of the maxima was  $3.30 \times 10^{-7}$  ampere. When it is noted that this was at a distance of 15 meters from the source of sound, it will be seen that the receiving apparatus possesses quite remarkable sensitiveness. Of course, too much importance must not be given to the distance from the source as a determining factor of the intensity, for, as will soon appear, this particular position, accidentally chosen, in the rear of the room was a position in which the sound was more intense than at many places much nearer to the source. However, even with a galvanometer of only moderate sensitiveness it was possible to extend the investigation satisfactorily to any part of the room. Curves of results at two other positions in the room are discussed below.

The question arises, how may we determine the exact region of space to which the indications belong? In Curve 1 of Figure 8 a maximum was found when the opening of the receiver was 5 cm. from the wall. Is the maximum of sound vibration at the opening of the cone, and, therefore, 5 cm. from the wall or is it inside the cone or outside the cone? Can we locate its exact position? In attempting to answer these questions it was decided to try the effect of reversing the telephone so that the opening pointed away from the wall. With the telephone thus reversed Curve 5 of Figure 8 was obtained. Unfortunately, on account of the size of the telephone and cone, it was not possible to extend the observations to points nearer the wall than 40 cm. The distance measurements for this curve were also made from the wall to the opening of the cone. By a comparison of this curve with Curve 4 we may get some evidence of the location in space of the sound vibration.

The two maxima of Curve 5 probably correspond respectively to the two right hand maxima of Curve 4, as is evidenced by their distance apart, and their relative amplitudes, and by the distance apart of the minima of Curve 5 as compared with the minima at 75 and 108 of Curve 4. Now it is seen by inspection that these two curves would be brought into coincidence as to location of maxima and minima, if, instead of having measured from the wall to the opening of the cone of the telephone, we had measured to a point 5.7 cm. outside of the cone; that is to say, the indications of the galvanometer are indications as to the relative amplitude of the sound vibration at a point 5.7 cm. outside of the opening of the sound-collecting cone.

While this reasoning is not entirely conclusive without further

evidence, because of the possible actual disturbance of the stationary system by the reversal of the telephone, yet the result seems highly probable on account of its agreement with the familiar fact that the maximum of motion of the air column of a tubular resonator is outside the end of the resonator. The sound-collecting cone of the present apparatus is a resonator for the pitch employed — in fact, the particular pitch was selected by a preliminary experiment which showed that the air column of this cone was in resonance with the pitch — and this resonant air column, according to deductions from the above experiment, is thrown into most active vibration when a region just outside (5.7 cm.) the opening of the cone is coincident with a region of large displacement.

This result enables us to locate the actual position of the nodes and loops of Curve 4, Figure 8. Each point of the curve belongs to a region of space 5.7 cm. nearer to the wall than the corresponding abscissa; therefore, the first maximum of motion, which was obtained with the opening of the cone 5 cm. from the wall, is really .7 cm. behind the wall, — that is to say, practically coincident with the wall.

In order to examine the distribution of sound intensity in the neighborhood of another portion of the wall of the room, the telephone receiver and its track were placed at 2 in Figure 7, and the galvanometer readings were taken with the opening of the cone turned toward the wall and placed at various distances from the wall. Curve 6 of Figure 8 was obtained as representative of the distribution at this position. Here again the corrected position of the first maximum is practically coincident with the wall. The interference system in this locality is much more irregular than in position 1, and the maxima with the exception of the maximum at 90 cm. are less intense than those at position 1. This is interesting when we note the fact that the distance of the position 2 from the source of sound is only one half as great as the distance of position 1. For hearing this particular note the position at the back of the room is more favorable than the much nearer position at the side of the room, notwithstanding the fact that the side position was directly in front of the lip of the pipe and was unobscured by intervening objects, while a line running from the source of sound to the position in the rear of the room passed immediately over the backs of numerous benches with which the room was furnished.

At a third position in the room, position 3, Figure 7, an interval of 100 cm. was investigated. The results obtained are shown in Curve 7, Figure 8. These distances (abscissae) are measured from an arbitrary origin. The opening of the cone of the telephone was

turned toward the spot marked "3" in the elevation drawing of Figure 7. Here again a fairly definite stationary system was found. This position is also less favorable for hearing this particular tone than the position 1 in the rear of the room.

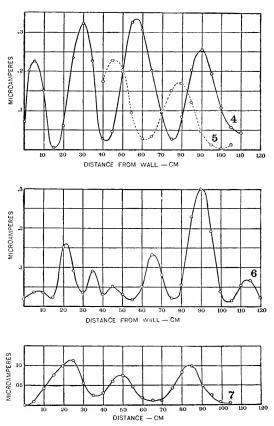


FIGURE 8. - Stationary waves in large lecture room.

These experiments were made in the large lecture room which is immediately over the machine shop of the laboratory, and were apparently not in any way affected by the very considerable vibration and noise of several motors and lathes in almost continual operation. The rectifier is, however, extremely sensitive to electric waves; and electric disturbances, when they happen to be in syntony with the rectifier circuit may prove troublesome. In the course of the present

experiments the breaking of a chronograph circuit by an electric clock in a distant room gave noticeable deflections. Most of these electric disturbances may be easily tuned out by a change of the inductance or capacity either in the disturbing circuit or in the rectifier circuit. By wearing a head telephone connected in series with the galvanometer during the observations, the observer may easily recognize any foreign disturbances by their characteristic tones in the telephone.

It was not the purpose of the present note to multiply observations on the acoustic properties of a particular room. However, apart from the interest attaching to the method of the experiment, the result that for a sustained tone, even in a large room, there are practically all over the room definite positions of sharp maxima and minima of intensity is rather a striking fact when brought out objectively. The results show that an auditor may sometimes greatly improve his hearing of a discourse or a musical rendition by a slight motion of his head so as to bring his ear into a position of maximum intensity. Perhaps he already unconsciously does this, which may account for the fixed attitude of an audience in close attention.

The occurrence of these definite maxima and minima of intensity of sound, due to reflection from the walls, should be borne in mind when one attempts to interpret any experiment on sound performed in a closed room. As Professor Sabine has repeatedly emphasized, the mere fact that the walls are distant from the source of sound, while the observer, or sound-receiving apparatus, is near to the source, is not sufficient precaution against the influence of reflection, because the reflecting surfaces are on all sides and act many times, and may combine in their action in such a manner as to be a very considerable factor in the resulting intensity.

The curves of Figure 8 are plotted in terms of current in the galvanometer. It was shown above, in Experiment II, how the indications of the galvanometer may be made independent of the rectifier by substituting voltage from the curve of Figure 6 for the corresponding current values. When this substitution is made, the proportional differences between the maxima and minima, expressed in voltage values, become somewhat smaller than these differences expressed in current values. However, on account of the intermediation of the telephone receiver between the sound vibrations and the electrical indications, it is still not possible, without further calibration of the apparatus, to obtain absolute or even relative values of the sound intensity. Several methods of obtaining this calibration in terms of sound intensity suggest themselves. One method is to employ the distance law in connection with experiments performed

in the open. Another method, which is perhaps more interesting, would be to study directly the characteristics of the magneto-telephone when used as a generator, by measuring directly the amplitude of vibration of the telephone diaphragm and then measure with the rectifier the resulting alternating voltage.

#### V. Sensitiveness of the Method.

The galvanometer employed in the above experiments was not particularly sensitive. Its resistance was decidedly too low and entirely inappreciable in comparison with the resistance of the rectifier. A galvanometer of the highest attainable resistance would hardly be appreciable in resistance in comparison with the resistance of the rectifier. Also the transformer employed between the telephone circuit and the rectifier circuit did not have high enough resistance in its secondary. With evident improvements in these respects the sensitiveness of the apparatus could be greatly increased, in case one should desire to measure extremely feeble sounds. However, without such improvements the sensitiveness of the apparatus seems to greatly exceed that of any of the physical methods heretofore employed for the measurement of sound.

For a deflection of .2 millimeters on the galvanometer scale, the power in the galvanometer circuit, calculated from the current-voltage curve of Figure 6, amounted to  $1.53 \times 10^{-5}$  ergs per second, while Lord Rayleigh <sup>4</sup> finds the minimum energy that will affect the human ear to be  $1.11 \times 10^{-5}$  ergs per second, for a pitch of 2730 vibrations per second. That is to say, with the apparatus of the present experiments, in order to get .2 mm. deflection it is necessary to develop energy in the galvanometer circuit at about the rate at which energy is received by the human ear at minimum audible intensity. On account of the inefficiency of the magneto-telephone receiver when used as a phono-electric generator, energy at a rate much greater than this is required by the magneto-telephone receiver in order that this amount of power may get into the electric circuits.

The use of a carbon transmitter in place of the magneto-telephone receiver for the sound receptor, while not so constant as the magneto-telephone, is of course enormously more sensitive. With this arrangement the condenser C of Figure 2 was replaced by a battery of four storage cells, and a transformer of lower resistance primary was employed. Preliminary tests showed that the galvanometer would then

<sup>&</sup>lt;sup>4</sup> Lord Rayleigh, Proceedings of the Royal Society, 1877, Vol. 26, p. 248.

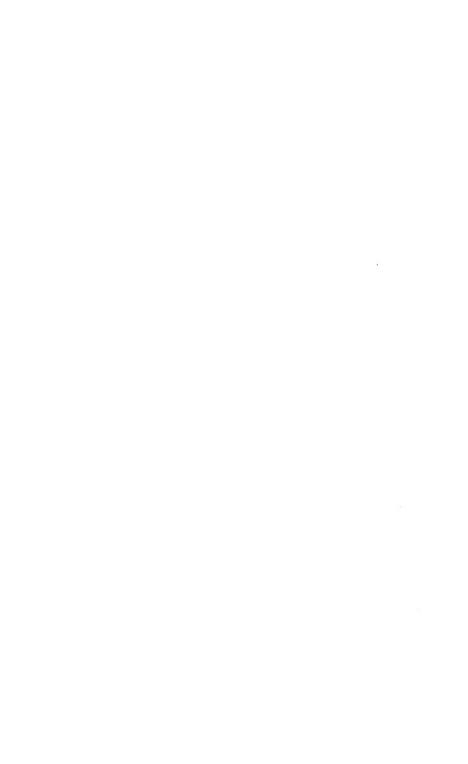
be thrown off the scale when a small organ-pipe was sounded almost anywhere on the same floor of the building, even when the passage of the sound from the pipe to the transmitter was through long corridors and several partly closed doors. With the pipe at P and the transmitter, without sound-collector, placed at 3 in the room shown in Figure 7, a delicate Weston ammeter gave a whole scale deflection, which corresponded to a current of 392 microamperes. With the use of this ammeter instead of the galvanometer readings could be taken with great rapidity and may be easily made self-recording.

To test further the sensitiveness of the apparatus with the carbon transmitter substituted for the magneto-telephone receiver, this transmitter was supplied with long leads and placed outside the building. An assistant was sent off across an open field. When the assistant blew a small organ-pipe,  $C_5$ , 1024, at a distance of 100 meters away, a deflection of 5 mm. corresponding to a current of  $3.06 \times 10^{-8}$  amperes was obtained. A locomotive whistle at a distance of perhaps a mile gave 75 millimeters deflection.

Jefferson Physical Laboratory, Harvard University, Cambridge, Mass. December 27, 1907.







## Proceedings of the American Academy of Arts and Sciences.

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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

## LONGITUDINAL MAGNETIC FIELD AND THE CATHODE RAYS.

BY JOHN TROWBRIDGE.



## CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

## LONGITUDINAL MAGNETIC FIELD AND THE CATHODE RAYS.

By John Trowbridge.

Presented December 11, 1907. Received January 6, 1908.

In a previous article on the Magnetic Field and Electric Discharges <sup>1</sup> I described various phenomena which occur under the effect of a longitudinal field, both at the anode and the cathode. The present article deals with the effects of the field on the cathode rays after they have passed into the region beyond the anode. The form of tube which contained the rarefied gas was similiar to that generally employed to study the canal rays: a cylindrical tube with a concave aluminium cathode, an iron anode with an orifice at its centre, and a prolongation of the cylindrical tube behind the anode. Two exactly similiar tubes of this form, equal in size, were connected by the same adjunct to the exhausting pump, and were, therefore, under the same pressure.

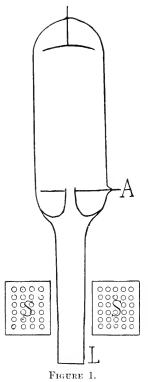
In one of these tubes (Figure 1) the back of the anode, or iron terminal, was completely shielded from the prolongation of the tube in which canal rays are usually studied. A glass tube passed through the orifice in the iron terminal and was welded to the walls of the prolonged larger tube. No rays could enter the canal ray region except through the orifice in the iron terminal. In the companion tube the back of the terminal was not protected, and rays could pass over the periphery of the iron terminal and also through the orifice at the centre of the terminal.

It was found that the tube (Figure 1) apparently reached a much higher state of exhaustion than the companion tube, which I shall call B, although they were connected by the same large adjunct to the pump and, therefore, there could be no question of slow transpiration. One tube, A, was close to the X-ray stage, while B was hardly beyond the stratification stage.

I replaced these tubes by two spherical bulbs (Figure 2) similar to those commonly employed as X-ray tubes; these tubes also had prolongations, or canal regions, similar to those of the previously mentioned

cylindrical tubes. In one, A, the back of the terminal was protected as in Figure 1; in the other, B, the back was not protected. The same phenomenon was observed. Tube A came up nearly to the X-ray stage, while the other was apparently far below this stage.

Figure 2 is a photograph of the state of the two tubes. It is evident that the mere appearance of the discharge between the terminals is no criterion of the state of exhaustion unless one carefully considers



the forms of the tubes and the extent of wall surface submitted to the bombardment of the cathode rays. The difference which I describe is probably due to the walls of the prolongation of the vacuum tubes, A being more protected from this bombardment than those of tubes B.

The forms A apparently showed the canal rays as perfectly as the forms B, when the iron terminal was made the cathode; and these rays did not seem to be modified by the protection of the edges of the orifice in the iron tube by the glass tube. The canal rays, therefore, come entirely from the space between the anode and the cathode.

A solenoid (S, Figure 1) was next slipped over the prolongation of the tubes. This prolongation, therefore, formed the core of the solenoid, and the rays passing through the orifice in the terminal could be submitted to a longitudinal magnetic field. By a proper adjustment of the position of the solenoid the cathode beam passing through the orifice in the iron terminal or the anode could be brought to a sharp focus on the end of the prolongation tube. This was also the case in tube B; but in the latter there was also a phosphores-

cent ring surrounding the focus of the central beam which was due to bringing to a focus the rays which passed over the periphery of the circular iron anode. The phenomenon of focusing or convergence of the rays is due to these rays seeking the weakest part of the magnetic field. The field formed by the iron disc terminal outside the solenoid, together with that of the short solenoid, had two channels in which the field was weakest: one through the orifice at

the centre of the iron terminal, the other around the periphery of this terminal.

It was to be expected that the Canalstrahlen could not be brought to convergence by this application of a longitudinal magnetic field. The phosphorescence of these rays remained unaffected.

### Phosphorescence of the Canal Rays.

In most cases the phosphorescence caused by the Canalstrahlen is similiar in color to that produced by the cathode rays. When, how-

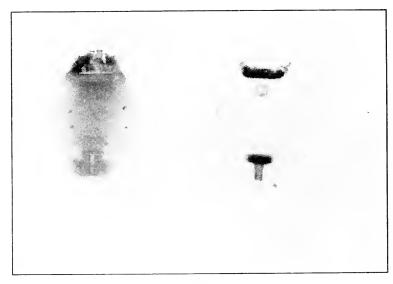


FIGURE 2.

ever, the Canalstrahlen fall upon lithium chloride, there seems to be a marked difference. Professor J. J. Thomson in his treatise on Conduction of Electricity through Gases <sup>2</sup> describes a form of tube in which a layer of lithium chloride can be bombarded alternately by both kinds of rays, and says that when the layer is struck by the Canalstrahlen it shines with a bright red light; the lines of the lithium spectrum are very bright, and when the direction of the discharge is reversed, so that the layer is struck by the cathode rays, its color changes from bright red to steely blue, giving only a faint continuous spectrum but not the lithium lines. The layer speedily becomes black in hydrogen.

<sup>&</sup>lt;sup>2</sup> University Press, Cambridge, 1906, p. 642, vol. XLIII. — 26

I have succeeded in producing the red phosphorescence by the cathode rays, thus annihilating the distinction, in this case, between the two kinds of rays. The method adopted seems to have a general application in the study of phosphorescence and is as follows:

The vacuum tube was of cylindrical form. Figure 1 shows the arrangement. A represents the circular iron terminal with its central orifice perforated by a glass tube; S, the solenoid; L, the ground-glass stopper with the layer of lithium chloride at its end.

When the solenoid is excited, the cathode rays can be brought to a sharp focus on the layer at L, and the apparatus can be called in popular language a magnetic lens. A very intense cathode beam can be made to converge at L by suitably adjusting the solenoid. The rays seek the weakest part of the magnetic field. Immediately on striking the layer of lithium chloride the red phosphorescence appears at the centre of the focus, and is surrounded by the blue phosphorescence; either the red or the blue can be produced at pleasure.

It seems, therefore, that if n is the number of cathode particles, m their mass, c their velocity, and n' the number of positive particles, m' their mass, c' their velocity, that the equation

$$nmr^2 = n^t m^t v^{t/2}$$

holds on the unit of area, and that the distinction, in this case between the color produced by the cathode rays and the Canalstrahlen disappears. The production of the two colors is a question of energy on the unit of area.

I have examined the phosphorescence of the other metals of the same group as lithium chloride. Caesium chloride gives a very bright blue color for both the cathode and the canal rays, and the blue lines of the spectrum appear with the application of the cathode beam. Rubidium gives both a red and a blue color; the red, however, is much less bright than in the case of lithium chloride. All of these salts are quickly decomposed. Calcium tungstate recovers from fatigue very quickly, and is not decomposed appreciably, even after long exposures. Its use for X-ray screens is therefore substantiated by these experiments.

Application of a Longitudinal Magnetic Field to X-ray Tubes,

In the article on the Magnetic Field and Electric Discharges,<sup>3</sup> I stated that the application of a longitudinal field at the anode might form a useful method of concentrating the cathode rays. Since this

<sup>&</sup>lt;sup>3</sup> These Proceedings, 28.

article was written I have studied the subject more carefully, and have devised a safe and practical method, which is analogous to that I have used in the study of the phosphorescence of the Canalstrahlen.

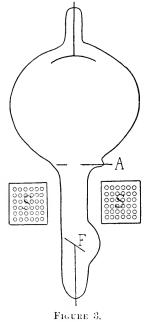
The form of tube is shown in Figure 1. A is an iron disc anode (Figure 3) with a perforation at its middle. S is a solenoid which can be adjusted along an appendix to the X-ray bulb. F is the usual focal plane of polished platinum. Opposite this focal plane the glass is blown thin to permit the egress of the X-rays. The cathode beam is brought to a focus at F by adjustment of

brought to a focus at F by adjustment of the longitudinal field of the solenoid.

The dimensions of the apparatus are as follows:

Diameter of the spherical bulb, 10 cm. Distance between the concave aluminium cathode and the iron disc anode, 6 cm. Length of the cylindrical appendix containing the focal plane, 10 cm. Internal diameter of the cylindrical appendix, approximately 3 cm. The outer diameter of the solenoid was 10 cm., the internal diameter 6 cm. Length, 4 cm. There were 10 layers of no. 18 wire, Brown and Sharpe gauge. The solenoid was excited by two or five storage cells. A narrower appendix and a smaller bulb opposite the focal plane would give a stronger field with less current.

When the cathode stream is made to converge by the solenoid on the focal plane F, the intensity of the X-rays is increased in a marked manner. Judging the intensity by the distance at which equal intensity is obtained with and without the magnetic



field, I have more than doubled the intensity of the X-rays by the application of the field. The method has the advantage of producing the X-rays from a sharp focus and should, therefore, give better definition.

It may be urged that the amount of energy employed in exciting the magnetic field could, with equal advantage, be added to that which excites the tube; but this would result in possible strain or danger to the tube and would not result in bringing the stream to a sharp focus. The large bulb need not be blown thin, and therefore the danger of perforation can be greatly lessened; moreover, the application of the mag-

netic field serves as a rectifier, and when a Leyden jar is used it allows only the oscillation from the cathode to reach the focal plane.

The canal rays appear to fatigue certain substances,—for instance, lithium chloride and rubidium chloride,—and after the application of these rays the blue phosphorescence of the cathode rays is diminished. It can, however, be restored by increasing the strength of the cathode beam. This can be accomplished by the following arrangement. A storage battery was connected to the exhausted tube through a large running water resistance, and a spark gap was inserted in the circuit. The coatings of a small Leyden jar were connected to the spark gap; the spark seemed continuous to the eye. Under the effect of the longitudinal magnetic field a very brilliant phosphorescence could be produced even after extreme fatigue of the group lithium, caesium, and rubidium chlorides. It is therefore probable that the cathode phosphorescence can be restored by stronger and stronger cathode rays condensed in the manner I have described.

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

## Proceedings of the American Academy of Arts and Sciences.

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# NOTE ON SOME METEOROLOGICAL USES OF THE POLARISCOPE.

By Louis Bell.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED, WHOLLY OR IN PART, WITH APPROPRIATION FROM THE RUMFORD FUND.



## NOTE ON SOME METEOROLOGICAL USES OF THE POLARISCOPE.

#### By Louis Bell.

Presented January 8, 1908. Received January 27, 1908.

This is merely a preliminary notice of certain facts regarding atmospheric polarization which may prove to have some prognostic value. They were incidental to a proposed study of the character of autumnal haze which the writer undertook last year at Mount Moosilauke, N. H. This peak, 4811 feet high, has an almost uninterrupted sweep of horizon over a radius of one hundred miles or so and offers an excellent chance for investigating the distribution and nature of the haze that veils the landscape in early autumn. For instruments I took along a Savart polariscope, merely a Savart plate with a bit of tourmaline as analyzer, an extemporized double-image polarimeter of the type outlined in the early and valuable paper of Professor E. C. Pickering, a couple of carefully calibrated photographic wedges for determining opacities, and a direct vision spectroscope.

A prolonged easterly storm, about the only thing which could have defeated the program, cut short observations upon the summit, but a week of preliminary observations at Breezy Point (elevation 1650 feet) at the base of the mountain yielded results which seem to be of sufficient interest to put upon record.

These were made mostly with the Savart polariscope, an instrument which, from its very wide field of view and great sensitiveness, showing even one or two per cent of polarization, enables sky conditions to be very readily investigated. The character of the sky polarization, with its general symmetry and maximum in a plane at 90° solar distance, is well known, but the nature and causes of its casual variations have not, perhaps, received the attention that is their due. Nearly everything in the landscape polarizes by reflection to a greater or less extent, the more as the specular component of reflection is the greater. For example, the glossy upper surface of a maple leaf polarizes strongly at fairly large angles of incidence, while the mat lower surface has only

a trifling effect — which facts explain the old observation of Spottiswoode that ivy leaves polarize particularly well. Grass, trees, stones, especially if wetted, all produce their effect, which, when sky polarization is cut off by white cloud, is generally a maximum in the vertical plane.

I have several times observed this terrestrial polarization carried up by reflection into low-lying cloud as noted by Pickering (loc. cit.), or even into near-by dense fog otherwise entirely neutral. A completely cloudy sky is otherwise practically free of polarization, but in a partially clear sky white cumuli commonly show some effects with the Savart plate, and light cirri often give bands almost as strongly as the clear sky. This may be due to the usually considerable height of cirri, — quite enough to allow noticeable polarization to have origin below them, — or to their letting through considerable polarized sky light from above, — a phenomenon which I observed from the summit station in the case of rather thin layers of cloud in which it was immersed.

One of the most striking features of the sky polarization observed from Breezy Point was the extent to which it appeared while originating over short stretches of air. Mounts Kineo and Cushman, about three miles distant and dark with a heavy growth of conifers, repeatedly showed strong polarization effects from intervening haze, and at times slopes within a mile brought out the bands, although less conspicuously. On several occasions the polarization on Kineo and Cushman was sensibly as considerable as on peaks at ten or fifteen miles distance. Similarly, in the brief observations on the summit, the Green Mountains and the almost effaced Adirondacks showed little if any more polarization than the peaks in the same direction in the middle distance, although the former were eighty to one hundred miles away and the latter only twenty to forty miles. These results follow from the exponential relation between distance and apparent absorption, but show clearly the magnitude of the effects due to comparatively short reaches of air.

At no time was I able to repeat the results obtained by Tyndall in the apparent clearing up of the haze by observation through a crossed Nicol. In this case the mountains remained dim, Nicol or no Nicol, showing that the typical autumnal haze, often whitish blue near the horizon, acts mainly by general obstruction and diffusely reflecting a good deal of light, the polarized component being usually only moderately strong.

Haze in general is well known to be due simply to suspended particles of one sort or another, and haze which produces polarization, as

well as the ordinary sky polarization, is well known to be due to particles, whether of dust or water, or of other nature, small compared with the wave-length of light. Lord Rayleigh <sup>2</sup> has given the theory of this action in considerable detail.

The polariscope integrates the effect of such particles along the line of sight, and this information may have considerable meteorological significance. The light-scattering particles which produce sky polarization are much finer than those which produce coronae and similar phenomena, with the beginnings of ordinary reflection. In artificial fogs the nuclei gradually grow from the polarizing dimensions to those which scatter white light and become visible. It is not easy to assign exact dimensions to the finer particles. They are quite certainly much less than a quarter wave-length in diameter, that is, say 100 µµ, and probably run very much smaller. From the very exhaustive work of Barus 3 it appears that the diameter of the particles to which visible fog and coronae in a fog chamber of laboratory dimensions are due range from .0005  $\mu$  upwards, those near this limit showing as fog, while the coronae began to form as the diameters reached 10  $\mu$  and above. The fog particles to which lunar coronae are due often rise to greater dimensions, 20 or 30  $\mu$ .

Now such fog particles are the preliminary to rain, which forms by the accretion of these particles to a size that readily falls; and it is well known that water vapor, even when saturated as shown by the psychrometer, will not begin to condense to visible fog unless in the presence of nuclei about which aggregation takes place. These may be of very fine dust, or even of water particles electrically charged to an extent that resists the surface tension that would otherwise premote Such charged aqueous nuclei may exist in unsaturated evaporation. air at very small diameters, down to 1 or 2  $\mu\mu$ , as has been shown by J. J. Thomson, 4 by Wilson, 5 and by others. Between these almost molecular dimensions and those indicated by coronae are the light scattering particles active in sky polarization. Their effect, that is, the amount of light scattered, varies, as Rayleigh 6 has shown, as the inverse fourth power of the wave-length of the light affected and directly as their volume, assumed to be small compared with a wave-length. Now plotting the resulting equation,  $I = \frac{\kappa A}{\lambda^4}$ , one obtains a group of curves

shown in Figure 1 which discloses the cause of the familiar intense blue

Phil. Mag., 1871, p. 107 et seq.
 Smithsonian Cont., No. 1373.

<sup>&</sup>lt;sup>4</sup> The Discharge of Electricity through Gases.

of the scattered light. As larger particles grow during the process of nucleation or are present as dust, the blue gets weak and whitish from the scattering of white light. Near the horizon, where the light

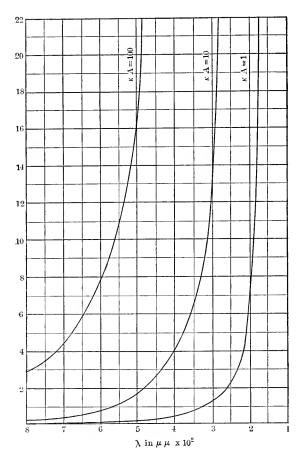


FIGURE 1.

traverses a long reach of atmosphere and coarser dust is common, one gets the familiar weakening of the sky blue.

The process of increasing nucleation, which results in cloud formation and frequently in subsequent rain, can be followed very closely by the polariscope. A fall in polarization, particularly when the spectroscope

shows the presence of much aqueous vapor, indicates the progress of nucleation.

On several occasions I noted this phenomenon in the Breezy Point observations. Starting with strong polarization on the distant hills to the southward and a strong rain band visible in the spectroscope, the next few hours showed a conspicuous weakening of the polarization, followed presently by the formation of visible clouds, and in at least two cases by precipitation. In short, if from change of temperature or other cause cloud is due to form in any particular direction, the nucleation which precedes visible fog formation is bound, other things being equal, to cut down the polarization. The prognostic value of this process depends largely upon the rate at which it progresses. In two instances which I noted, the decrease toward the south occupied most of an afternoon. Of course a drifting in of coarser dust particles would produce weakening of polarization, but the concurrence of weakening with a heavy rain band intimates very strongly that nucleation is progressing.

A detailed study of the changes would require the use of a sensitive polarimeter, by which variations from the theoretical polarization could be accurately measured. Observations of this kind, made where there is a wide sweep of horizon, should frequently disclose incipient cloud formation and the causes which produce it. The use of a spectropolarimeter would be very desirable, as showing by the change in the quality of the scattered light the progress of events. The nature of the minute nuclei, whether dust or water particles, is not definitely After a heavy rain storm the lower strata seemed to have been cleared pretty effectively of polarizing nuclei, while the upper sky remained much as before. On one occasion, more than twenty years ago, I was taking rain band observations on Moosilauke and was favored with a day in which the distant peaks, even up to one hundred miles, stood out almost as black as silhouettes, while the sky took on a deep hue almost startling in its unfamiliarity. A polarimeter would certainly have given extremely interesting results had it been at hand. It seems quite possible that one might get a fairly clear idea of the relative number and distribution of nuclei in the upper air by such means.

It would certainly be interesting also to find out whether the apparently very strong absorption of ultra-violet rays by the atmosphere is due to any genuine absorption or merely to a serious loss of light by lateral scattering, which Rayleigh has shown may perhaps be due to the air molecules themselves. In the lower strata my observations pointed rather to dust than to minute water nuclei, since a whitish

haze showed powerful polarization on near-by peaks, making it clear that the haze was extremely heterogeneous. The conditions which would produce stable water nuclei of strongly polarizing size on a clear day would tend to reduce larger droplets to the similar order of magnitude instead of leaving them to superimpose specular reflection.

I am not disposed to suggest that in the polariscope we have a meteorological tool of vast importance, but my preliminary observations certainly show that it gives a most instructive view of the very early stages of atmospheric nucleation, and especially if combined with rainband observations it should have material prognostic value as regards comparatively local conditions. There is also a chance for forming a clearer idea of the conditions of nucleation in the upper air, including the very high altitudes, since polarization is manifest after the sun is so far below the horizon as to illumine only the upper strata. I bring the preliminary facts to notice here in the hope that some one with a suitable location and opportunity for systematic observation may find them useful as a guide to further work along this line.

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CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE. E. L. MARK, DIRECTOR.—No. 195.

THE SENSORY REACTIONS OF AMPHIOXUS.

BY G. H. PARKER.



CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE. E. L. MARK, DIRECTOR.—No. 195.

## THE SENSORY REACTIONS OF AMPHIOXUS.1

### By G. H. PARKER.

Presented March 11, 1908. Received March 5, 1908.

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#### 1. Introduction.

Whatever position may be assigned to amphioxus in the classification of the chordates, it is now generally admitted that this animal retains many of the more primitive features of the ancestors of the vertebrates. Such features not only occur in its anatomy and embryology, but are to be expected in its activities. As the structure of amphioxus throws light on the complex organization of the vertebrates, so its activities, may give some indication of the way in which the more complex functions of these animals have come into being. It is from this standpoint that I have undertaken the study of the sensory reactions of amphioxus.

The material upon which this work was based is the so-called West Indian amphioxus or lancelet, Branchiostoma caribbaeum Sundevall, a close relative of the common European form, B. lanceolatum (Pallas). This material was collected and studied during the summer of 1905 while I was at the laboratory of the Bermuda Biological Station located at Hotel Frascati, Flatts Village, Bermuda. The living

<sup>&</sup>lt;sup>1</sup> Contributions from the Bermuda Biological Station for Research, No. 12.

lancelets were obtained from the Flatts Inlet, which leads from the outer waters to Harrington Sound. This inlet, through which a strong tidal current is almost always running in one direction or the other, contains long stretches of coarse coral and shell sand, and it was in these sandy stretches, especially near the open mouth of the inlet, that the lancelets were found in abundance. They likewise occurred, as recorded by Barbour (:05, p. 110), in the sandspit near the inner end of the inlet opposite Hotel Frascati, but they were by no means so abundant there as in the coarse shelly stretches which were near the outer mouth of the inlet and at low tide were still covered by several feet of water. From this source, with the assistance of some of the negro boys from the neighborhood, a daily supply of large, vigorous lancelets was obtained, and, as the animals were available in the laboratory almost immediately after they were caught, the conditions were unusually favorable for a study of their sensory reactions. For experimental purposes these lancelets proved to be very satis-They could be kept for a number of days in a vigorous condition in large glass jars containing sea water and some coral sand. provided that from time to time the sea water was renewed, and their resistance to the adverse conditions of operative experiments was as great as that of B. lanceolatum (Haeckel, '80, p. 141).

In the shoal water of Harrington Sound northwest of Trunk Island the expeditions from the laboratory on several occasions dredged Andrew's lancelet, Asymmetron lucayanum Andrews, but this species was not sufficiently accessible nor abundant to make it a satisfactory form for experimentation. In testing the sensory reactions of the lancelets I therefore limited my work to the more common species, Branchiostoma caribbaeum, and attempted to determine the reactions of this species to light, to heat, and to mechanical and chemical

stimuli.

## 2. Light.

Although the sensitiveness of amphioxus to light was known to Costa ('39, p. 4)<sup>2</sup> and many other earlier investigators, and has since been generally admitted, much difference of opinion has been expressed as to the degree of this sensitiveness. Willey ('94, p. 10) declares that "if a lighted candle is carried into a dark room in which amphioxus are being kept in glass jars, the excitement produced among the small

<sup>&</sup>lt;sup>2</sup> The statements concerning the reactions of amphioxus to light given by Costa do not occur in his first account of this animal (Costa, '34, p. 49) as cited by Krause ('97, p. 513), but in his later and more lengthy description (Costa, '39, p. 4).

fish is indescribable," and Nagel ('96, p. 79) states that "plötzliche Belichtung lässt dann die sämtlichen Exemplare wild durchs Wasser jagen." Hesse ('98°, p. 461) confirms these observations and records that light calls forth vigorous swimming. On the other hand, Nüsslin ('77, p. 23), who also tried sudden illumination, affirms that amphioxus is only very slightly sensitive to light, and Rohon ('82, p. 38) expresses the belief based on experimental evidence that the so-called light reactions of this animal are really reactions to heat, and that it is not sensitive to light at all, or at most only to a very slight degree, — an opinion concurred in by Kohl ('90, p. 185).

In consequence of this difference of opinion the first question to be settled was, whether amphioxus was or was not sensitive to light. therefore repeated the experiments made by Willey, Nagel, and Hesse, and with confirmatory results. When sunlight, daylight, lamplight. or even candle-light was allowed to fall into a previously darkened glass dish containing a dozen or more amphioxus, the whole company swam about for a minute or so in wild confusion and then dropped as though exhausted to the bottom. At first sight this seemed to be conclusive evidence of the great sensitiveness of amphioxus to light, but a more careful scrutiny of the steps in the experiment showed that this was not necessarily so. When light first fell upon the dish, all the lancelets did not begin at once to swim about excitedly. usually happened was that a few moved slightly, and in doing so they touched others; these then sprang suddenly into active locomotion, and in an instant the whole assembly was swimming in wild confusion. Thus it would seem that, while light was the initial stimulus for a few individuals, the wild and excited swimming which gave the impression of great sensitiveness to light was not due directly to this factor, but to mechanical stimulation caused by mutual contact.

To test this hypothesis I placed a shallow dish of sea water containing twenty live amphioxus in a dark room and, after about an hour, I threw upon it the light of a strong lamp; in a few seconds all the animals were swimming as though in the utmost excitement. I then let them rest in the dark for a full hour, whereupon, without illuminating the dish, I felt for one with a glass rod, and, having touched it, I soon heard an agitated movement in the dish such as had followed the previous sudden illumination. Upon turning on the light the animals were found to be in as much commotion as at the trial in which light had been the initial stimulus. I then took the twenty animals that had been used in these two experiments and put each one in a separate dish of sea water and placed each dish in an approximately light-proof compartment by itself. After an hour I

illuminated dish by dish in turn with the same lamp that had caused the whole assembly of lancelets to swim wildly about when together, and noted the individual reactions. Of the twenty animals tested, twelve reacted, some more, some less, but none vigorously; eight absolutely failed to give any response whatsoever, even after continued illumination. The twenty animals were then placed together in a single glass dish, and, after about an hour, they were suddenly subjected to bright illumination, with the result that they exhibited the same commotion as was seen in the first of these experiments. I therefore conclude that the wild swimming recorded by Willey, Nagel, and Hesse is not, as they believed, evidence of great sensitiveness to light, but is the result of the mechanical stimulation of one amphioxus touching another, and that amphioxus, as stated by Nüsslin, is really only very slightly sensitive to light.

Rohon's belief that the so-called light reactions of amphioxus are really reactions to radiant heat is not supported by my observations. Contrary to the statements of Rohon, amphioxus is responsive to light that has passed through a heat screen; nor does Rohon seem to have been aware of the fact, pointed out later by Krause ('97, p. 514), that a few centimeters of sea water is as effective a heat screen as the alum solution that he used, and that consequently in all his experiments that were carried on with some depth of sea water, the animals that were supposed to be subjected to radiant heat were as a matter of fact as completely shielded from it as though they were behind an alum screen. Kohl's concurrence in Rohon's opinion does not seem to be founded on any observations of his own, for he ('90, p. 182) states that he had no opportunity to work with living material. I therefore believe that the slight initial locomotor response that amphioxus usually makes when a beam of light is suddenly thrown on it is dependent upon the light waves themselves and not upon radiant heat.

Although amphioxus is assuredly not so sensitive to light as many investigators have supposed it to be, it does show a capacity to respond to a considerable range of this form of stimulus. Nagel ('96, p. 80) stated that its characteristic reactions could often be called forth by a relatively weak stimulus, such as the diffuse light of a cloudy day. In my own experience animals that have been kept in the dark for some time will usually react to light of not more than a few candle-meters intensity, but the same individuals after lengthy exposure to ordinary daylight will often fail to respond to a beam of strong sunlight. Obviously the capacity of the animal to respond to light is more or less determined by its previous condition, its sensi-

tiveness diminishing with continual exposure to light and increasing when the light is excluded from it. But even under the most favorable circumstances the reactions to light as compared with those to other kinds of stimuli are relatively slight in amplioxus.

Although amphioxus shows much diversity as to the intensity of light to which it will react, in another respect its responses to this form of stimulus are very uniform. In all the tests I carried out, I never observed a reaction to a rapid diminution of light, and the reactions to light that did occur were always the result of a rapid increase of intensity. When an animal was resting quietly on its side in a shaded aquarium and a beam of sunlight was suddenly thrown upon it, it would usually respond by one or two vigorous locomotor leaps, after which it might come to rest even in the sunlight. If now the sunlight was suddenly cut off, no response followed. That this failure to respond was not due to exhaustion from over-exposure to light was easily shown by quickly throwing on the sunlight a second time, whereupon a reaction much like the first one usually followed immediately. In fact, a moderately rapid alternation of full light and shadow was generally followed for a number of times by reactions to the light and no reactions to the shadow till, after numerous trials, the animal ceased to respond at all. Amphioxus is therefore stimulated only by such rapid changes of light intensity as involve an increase in the illumination. This agrees fairly well with Nagel's statement ('94, p. 811; '96, p. 80) that sudden shadow calls forth from amphioxus either faint responses or none at all. In my experience the latter part of this statement is correct.

Having ascertained that amphioxus is sensitive to light, the next question that naturally arises is what portion of its body serves as the receptive organ for this stimulus. Numerous answers have already been given to this question. The conspicuous pigment spot at the anterior end of the nerve-tube discovered, according to J. Müller ('39, p. 198), by Retzius, was held by the former ('44, p. 95) and many other investigators to be a primitive eye. Hasse ('76, p. 287) believed that the light receptors were two lateral patches of integumentary cells, one on each side of the flattened anterior end of the animal. Nüsslin ('77, p. 25) was of opinion that the extreme anterior portion of the dorsal fin was the part sensitive to light. Krause ('88, p. 136), who discovered in the substance of the nerve-tube a pigment that he believed resembled visual purple, was thereby led to assume that this tube was the receptive organ for light. Nagel ('94a, p. 811) claimed that the whole outer skin was receptive to light. Hesse ('98, '98b) maintained that the numerous small pigment spots of the nerve-tube were each a

single eye comparable to the eye of a planarian; and to these Joseph (:04) added certain large cells in the anterior part of the tube which, from their structure, he believed also to be light-receptors.

To ascertain what part of the body of amphioxus is sensitive to light, I had planned to use local stimulation, and with this in view I arranged an acetylin light with a condensing lens and a pinhole diaphragm, so that I could have at command a small beam of strong light with which to test locally the various parts of the animal's body. Unfortunately the strongest artificial light that I could get was insufficient to call forth an invariable reaction, and I was at last driven to use concentrated sunlight for this purpose. This was obtained by mounting a mirror in an open space adjacent to the laboratory, and so directing it that a horizontal beam of sunlight was thrown through a window into the laboratory. This beam of light was screened of its heat by being made to pass through seven centimeters of water contained in a glass vessel with flat sides, and it was concentrated by a large lens whose principal focus was about twenty-five centimeters. A few centimeters nearer the lens than its principal focus and in the cone of concentrating light, an iron diaphragm with a pinhole was placed that intercepted all the light except that which passed through the pinhole. In this way a well-circumscribed minute beam of intense light was obtained, and by means of this beam the body of the amphioxus was explored while it rested in a glass dish of sea water with flat sides. It was found by experiment that the dish containing the amphioxus could be moved about with considerable freedom without disturbing the animal. In this way the beam of light was brought to bear on any desired part of the animal's body.

My first experiments were directed toward ascertaining the value of the so-called eye-spot at the anterior end of the nerve-tube as a receptive organ for light. Experiments had already been made on this organ by Nagel ('94°, p. 811; '96, pp. 40, 80), who recorded that after the animal's anterior end, including the eye-spot, had been cut off, the lancelet was found to be as sensitive to light as ever, a condition confirmed by Hesse ('98°, p. 461). I repeated this experiment on six lancelets. All were first tested with light and found to respond when suddenly illuminated. The anterior tip of the body with the eye-spot was then cut off, and after an hour all were tested again. I was unable to distinguish in this second test that the lancelets were any less sensitive to light than before the removal of the eye-spot, and my results thus confirm those of Nagel and Hesse.

Although these results demonstrate conclusively that the so-called eye-spot is not essential to the light reactions of amphioxus, they do

not show that this spot may not be a light-receptive organ. To test this possibility I attempted by means of the minute beam of light already described to illuminate the spot exclusively, and to see if a reaction resulted. This was by no means easily done, for the spot is so small that its position in the living animal cannot well be observed directly, but must be surmised. Furthermore, when the light enters the substance of the animal, it becomes much scattered, and hence may reach other parts than those it is intended to illuminate. Nevertheless, it was possible on a number of animals to throw intense light on the eye-spot without getting a response, though, when the light was moved to a position somewhat posterior to the spot in question, a vigorous response followed. I therefore conclude that not only is the so-called eye-spot of amphioxus unessential to its light reactions, but that this organ is in no sense a light-receptor. These physiological results, then, support the view long ago advanced by Stieda ('73, p. 51) on the basis of anatomical evidence, that this spot is not a visual organ. For this reason I shall in future call it simply the anterior pigment spot, though its nervous nature seems well established by the recent work of Edinger (:06). In a similar way I tried to get reactions from lancelets by directing the beam of light on the flattened sides of their anterior ends, where, according to Hasse ('76), light-receptive organs were supposed to be located. In no instance did I get a reaction, and I therefore agree with Nüsslin ('77, p. 12) and with Kohl ('90, p. 183) in denying the existence of light-receiving organs in this region.

Lancelets from which the anterior end of the dorsal fin had been removed were as sensitive to light as before the removal, nor did normal lancelets react to the small beam of light when it was thrown on this part of the fin. I therefore believe that Nüsslin ('77, p. 25) was in error when he declared that the anterior end of the dorsal fin was the portion of the animal that was sensitive to light.

The part of the body of amphioxus that can be stimulated by light extends from a point a little behind the anterior end posteriorly to the tip of the tail. A beam of concentrated sunlight thrown across the body in any region between these two points always elicits some response. Krause ('97, p. 514) states that the anterior end somewhat distal <sup>3</sup> to the anterior pigment spot is most sensitive to light, and that the tail end is not sensitive at all. My results, as already stated, are almost precisely the reverse of these. I have found the anterior end, both in front of the anterior pigment spot and at least immediately posterior to it, insensitive to light, and the tail end extremely sensi-

<sup>3</sup> By distal Krause means, judging from the context, posterior.

tive. As Krause in his first description of the animal ('88, pp. 132 135) stated that it rests with its *tail* out of the sand, and in his later account ('97, p. 513) that the *head* usually projects, a fact well established since the time of J. Müller ('41, p. 399), is it not possible that in his study of the light reactions of this somewhat ambiguous form Krause has fallen into the not unnatural error of confusing the ends?

The extent of the region that is sensitive to light in amphioxus very nearly coincides with that of the nerve tube, and evidence obtained by local stimulation points to this structure as the part of the animal stimulated by light. Krause ('88, p. 132; '97, p. 513) has advanced the opinion that the bluish coloring matter that appears in the walls of the tube when this structure is treated with alkali is similar to the visual purple of the retina, and is in this way connected with the light receptive function of the tube. On treatment with alkali this coloring matter, according to Krause, becomes visible around the pigment spots in the tube, and among these are included the anterior pigment spot as well as the series of smaller spots that extend through almost the whole length of the tube; but it has just been stated that by local stimulation the anterior pigment spot can be shown to be insensitive to light, and since this coloring matter is as characteristic of that spot as of the other spots in the tube, I do not believe that the blue substance described by Krause has any essential connection with the light-receptive apparatus. As Hesse ('98', p. 556) has pointed out, Krause's belief that the blue is analogous to visual purple is unsupported by any good evidence, for this material shows no such relation to light as is characteristic of visual purple. It therefore seems to me that Krause's view is untenable.

Since amphioxus shows no response when strong light is thrown on the anterior end of its nerve-tube in front of the third or fourth segment, a region in which occur certain large cells supposed by Joseph (:04, p. 21) to be sensitive to light, I conclude that these cells are not open to that kind of stimulation and that the light-receptive organs must lie posterior to this region.

Although it is impossible, for reasons already given, to illuminate amphioxus locally with great precision, the exact portion of the animal that is stimulated by light can be determined with fair accuracy. This portion corresponds to the region in which the nerve-tube contains the small eye-cups described by Hesse. This correspondence is so precise that it seems very probable that these organs are the true photoreceptors. It must not be forgotten, however, that, in all regions where light has proved stimulating, this agent in its passage into the more or

less transparent animal first penetrates the skin, and it is not impossible that the receptive organs for light really lie in this layer, as maintained by Nagel ('94°, p. 811) and Jelgersma (:06, p. 390). This opinion is strengthened by what has recently been made out concerning the sensitiveness to light of the skin of certain reptiles, amphibians, and fishes, particularly ammocoetes (Parker, :03°, :05b).

Since I was unable to devise an experiment whereby the nerve-tube in amphioxus could be illuminated without having the light pass through the skin, I cannot be absolutely sure where the light-receiving organs lie, but there is a certain amount of indirect evidence on this question, all of which points in one direction. As has already been shown, the skin on the anterior end of the animal is not sensitive to light, this form of sensitiveness beginning posteriorly at no special region so far as the skin is concerned, but exactly where the eye-cups first occur in the This evidence, so far as it goes, favors Hesse's view that these eye-cups are the true light-receptive organs. Another piece of evidence has to do with the exact distribution of the animal's photoreceptiveness and that of the eye-cups. If different regions on the length of a lancelet are tested for their sensitiveness to light, they will be found to vary considerably. The most sensitive region is that which extends from a point several segments behind the anterior tip of the nerve-tube posteriorly over about one quarter of the length of the animal; the region next in sensitiveness is the most posterior quarter of the animal; and the least sensitive part of the whole region which is at all sensitive is approximately the middle half. In a series of trials in which was determined the relative intensity of the minimum amount of light necessary to stimulate in these three regions, it appeared that, if the minimum intensity for the anterior portion, the most sensitive part, is called 1, that for the posterior part was 1.5, and for the middle part 25.0, while an intensity of 0.5 was not stimulating to any part of the animal. If, now, the distribution of the eye-cups described by Hesse be taken into account, a striking correspondence to the sensitiveness to light will be found. In Branchiostoma earibbaeum the most anterior eye-cups occur in the third segment, and the remaining cups form a more or less segmentally arranged series reaching to the last segment of the body, which is practically the tip of the tail. In this series, so far as numbers are concerned, three general regions can be distinguished. The first region, the one in which the cups are most numerous, extends from about the fourth segment to about the twentieth; the region second in abundance covers about the last twelve segments of the body; and the third region, or the one in which they are fewest, is the middle portion of the body between the two regions

just defined. Hesse ('98', p. 457) states that in Branchiostoma lanceolatum the eye-cups are most abundant anteriorly and diminish in numbers posteriorly, till in the tail there may be not more than one cup to a segment. But this description, as Boeke (:02, p. 352) and Joseph (: 04, p. 18) have noted, is somewhat defective. In five specimens of B. lanceolatum from Naples that I have examined, the distribution was essentially like that in B. caribbaeum, in that, in addition to the considerably increased number of cups anteriorly, there was also an increase in the number in the tail region. This confirms Joseph's statement (:04, p. 18) for this species and agrees with the discovery of Boeke (:02, p. 352), that in young pelagic individuals of B. lanceolatum there are to be seen two groups of eye-cups, one anterior and the other posterior, corresponding to the two concentrations men-These two groups presumably unite later to form one series. The general plans of distribution of the cups in the two species, then, undoubtedly agree, and, since these plans of distribution correspond to the different degrees of sensitiveness to light for the different parts of the body in B. caribbaeum, I believe that the eye-cups described by Hesse, and not the skin, are the light-receptive organs.

In Branchiostoma caribbaeum, as in B. lanceolatum according to Hesse ('98', p. 458) and Boeke (:02, p. 351), the ventral eye-cups, as well as those of the right side, point in the main ventrally, while those of the left side point mostly dorsally. Hesse states further that in B. lanceolatum the caps of the two sides tend toward the right, and he suspected that this might be correlated with a possible habit of resting on a particular side. But in testing this hypothesis Hesse ('98', p. 459) found that the animals rested about as frequently on one side as on the other, and he therefore abandoned it. In B. caribbaeum I could not see that the cups were directed more toward the right than toward the left, but it was apparent that the majority pointed ventrally. This position seemed to me entirely consistent with the habits of this species. for it naturally lies in the sand with the ventral side obliquely uppermost, the majority of eyes being thus directed toward the most probable source for light. However, individuals that were in a glass dish without sand were, so far as I could see, equally sensitive to light falling on them in any direction.

If the light-receptive organs in amphioxus are the eye-cups of the nerve-tube, any part of the animal containing these organs might be expected to retain its sensitiveness to light. Nagel (94°, p. 811; 96, p. 79), after cutting these animals in two transversely, found that both halves still reacted promptly to light, but less energetically than the whole animal did. Krause (97, p. 514) declared that after halving

amphioxus the posterior part is much less reactive to light than the anterior, and Hesse ('98', p. 462), who repeated these experiments, could get only a trembling response to light from the anterior half and no response at all from the posterior one. My own results agree exactly with those of Hesse. I tested six fresh animals with strong sunlight, and, having found them sensitive to it, I cut each one transversely in two. After an hour, and again after two hours, I tested them with strong sunlight: the anterier halves always trembled markedly, but I could perceive no reaction at all to light from the posterior halves. When, however, I touched the posterior halves with very dilute nitric acid in sea water, they sprang and wriggled forward through the water most energetically, showing that they were still capable of active re-I am therefore convinced that cutting the animal in two has a profound effect upon its powers of reaction to light, greatly diminishing this capacity in the anterior half and practically nullifying it in the posterior half.

Although amphioxus reaets to light thrown upon almost any part of its body except the anterior end, its reactions are characteristically different in accordance with the region stimulated. When light is applied to the sensitive anterior fourth of the body, amphioxus almost invariably gives a vigorous backward spring, often accompanied with backward swimming. If light is applied to the less sensitive middle portion of the body, there is usually a slight backward spring, but sometimes the animal simply curls the body slightly. If the light is applied to the most posterior fourth, the animal almost invariably springs forward. In extreme cases, at least, the resulting movement is the most effective one for removing the animal from the source of This is still more clearly seen when a beam of strong stimulation. light parallel with the longitudinal axis of the amphioxus is directed against its anterior or its posterior end. In the former case the animal darts backward, and in the latter forward; in each instance it moves away from the source of light. For animals generally backward swimming is unusual, since the majority of negatively phototropic animals when illuminated from in front first orient by turning the anterior end away from the light before they begin active locomotion, whereas in amphioxus the locomotion is executed without the initial step of orientation. The case is parallel to that of a positively phototropic pycnogonid described by Cole (: 01, p. 201); this animal moves toward the source of light either with the anterior or the posterior end first. In the pycnogonid, however, the two kinds of movement are associated with somewhat different types of locomotion, for the animal swims backward toward the light or creeps forward toward it, whereas in amphioxus the reaction in both cases is simply swimming.

As a result of such a system of reactions, Branchiostoma caribbaeum falls under the head of negatively phototropic animals, and this is also the case with B. lanceolatum, which, according to W. Müller ('74, p. 7) and others, avoids light as far as possible when in captivity, and with Asymmetron lucayanum, whose habit, according to Andrews ('93, p. 214), is to collect on the side of the dish away from the light. Evidence of the same kind is also at hand for B. caribbaeum. If, into the middle of a large square glass vessel so placed that the sunlight falls obliquely into it through one side, living lancelets are dropped one by one, they fall to the bottom as a rule without response, whereupon they often begin swimming, and in practically every trial come to rest near the side of the glass away from the sun.

If a large glass aquarium is arranged so that one side and the halves of the two ends adjacent to it, as well as the corresponding portion of the top, are covered with light-proof paper and a number of amphioxus are allowed to swim freely about in it, they will be found during the day resting almost exclusively on the bottom of the darkened part, whereas during the night they will be found about equally distributed over the bottom.

Since amphioxus swims away from a source of light, it is negatively phototropic (Parker, :06, p. 61), and, since it is active in the light and comes to rest in darkened situations, it is photokinetic (photodynamic).

Light acts on amphioxus in a distinctly local way, and not as it does on animals, like most vertebrates, which possess eyes capable of forming images. This power enables a vertebrate to discriminate at a distance areas of light from areas of shade in a general field. If an amphioxus lying quietly in deep shade is stimulated to locomotion by a minute beam of strong light, it will dart off in almost any direction irrespective of the shadows and lights about it. Should it by accident come into the sunlight, it usually continues to swim; should it come into shade, it usually comes to rest. The light about amphioxus has little or no influence on the animal except when it falls with full intensity on the animal's body. This is dependent upon the fact that amphioxus is not very sensitive to light, and therefore reflected light of low intensity does not stimulate it, and, further, that the light-receptive organs of the animal have no adequate means for the formation of images.

Under ordinary conditions amphioxus is buried in the sand, excepting for one end. Which end this is has been a matter of some dispute. Yarrell ('36, p. 468) stated that the specimen from which he took his description was found by Mr. Cough with its tail sticking out from under a stone; and Steiner ('86, p. 497) declared that the animal

usually rests with its tail out of the sand, a statement repeated by Krause ('88, pp. 132, 135). Subsequently and without explanation both Steiner ('88, p. 41) and Krause ('97, p. 513) abandoned this opinion for the opposite one. That the animals ordinarily rest with the anterior end out of the sand was the opinion of J. Müller ('41, p. 399; '44, p. 84), Nüsslin ('77, p. 18), Rohon ('82, p. 37), Willey (94, p. 9), Nagel (96, p. 79), and others, and any one who earefully inspects a number of lancelets at rest will soon be convinced that this is the normal position. Although the extruded anterior end is the portion of the animal least sensitive to light, lancelets in their resting positions in ordinary sand will respond quickly enough to this stimulus. Thus in a large dish of coral sand, over which there were a few inches of sea water, the anterior ends of twenty-three lancelets were counted in dim light. As a result of throwing on a beam of very strong light, most of the heads were quickly withdrawn under the sand, only two remaining visible. This reaction is doubtless dependent on the stimulation of the most anterior eye-cups, and as a rule the resting position of the animal is such that this naturally occurs.

The negative phototropism of amphioxus has led to the belief that during the day it remains buried in the sand, except perhaps for its anterior end, but that during the night it leaves the sand and leads a more active existence. W. Müller ('74, p. 7) states that Branchiostoma lanceolatum is nocturnal, and at twilight comes to the surface of the sandbank in which during the day it is buried. Rice ('20, p. 9) mentions that individuals of this species which were seen swimming at night in the Naples Aquarium were quiescent in the daytime, and Rohon ('82, p. 36) and Krause ('97, p. 513) also speak of this species as having nocturnal habits. B. earibbaeum showed no evidence of such habits. All inspections of the aquaria that I made after nightfall, and with caution as far as light was concerned, demonstrated that the lancelets remained in the same position in the dark as in the light. Further, several glass vessels containing coral sand and known numbers of lancelets that were sunk over night to the natural level of the sand in the bed of the inlet, contained, when taken up the next day, the same numbers of animals, thus indicating that the lancelets had remained buried and had not come out on the surface of the sand, where the current would surely have swept them away, even supposing that they had not started swimming. Although this experiment was tried only a few times, the results always led to the same conclusion, and it therefore seems probable that at least B. caribbaeum is essentially a burrowing animal, and that it leaves its native sand only when forced to by the accidental action of currents, etc.

#### 3. HEAT.

The reactions of amphioxus to heat have been scarcely more than touched upon by the numerous investigators who have studied the reactions and habits of this animal. As has already been pointed out, the opinion of Rohon ('32, p. 38) and of Kohl ('90, p. 185), that the light reactions of amphioxus are really reactions to radiant heat, is erroneous; moreover it is not to be expected that animals like amphioxus, which live always under some depth of water, would have any special organs for the reception of radiant heat, since such heat penetrates water only a centimeter or two and hence would almost never reach these forms. The kind of heat that is a factor in the environment of amphioxus is the molecular vibration such as we recognize in the temperature of water, and this certainly has a distinctly circumscribing influence on the lancelets.

In testing the effect of heat on amphioxus, the temperature of the water in which they were living in the Flatts Inlet, 31° C. (July, 1905), was taken as the normal, and two series of experiments were conducted, one at temperatures above this and another at temperatures below it.

When lancelets were transferred from sea water at 31° C. to sea water at 35° C., they responded by darting about several times and then sinking quietly in the characteristic way to the bottom of the dish. Their subsequent reactions were essentially normal.

When transferred to sea water at 37° C., they made several quick darts, and finally fell quietly to the bottom, where they rested. When under these circumstances dilute acid was applied to them, they were found still to be actively responsive.

When transferred to water at 40° C., they made one or two sudden plunges, after which they dropped to the bottom, while their semi-transparent substance gradually whitened. When touched with dilute acid, the animals quivered slightly, but did not react otherwise. In a short time they were dead.

At 42° C. the animals darted once or twice, whitened quickly, and dropped to the bottom dead. Bert ('69, p. 21) states that water at 41° C. kills amphioxus in two minutes.

At 45° C. no locomotor response at all was given, and the animals began to whiten at once; they were apparently dead before they reached the bottom of the dish.

It is plain from these records that heat has at least two influences on amphioxus. It stimulates them to momentarily vigorous locomotion, and it also brings about death by the coagulation (whitening) of certain materials in their living substance. The coagulation begins apparently at about 40° C., and may be so rapid at 45° C. as to prevent the characteristic locomotor reaction which occurs at lower temperatures.

Having ascertained something of the general effect of heat on amphioxus, I next endeavored to determine what parts of its body were sensitive to this stimulus. To this end I used a temperature 39° C., a little lower than that which caused coagulation. I attempted to apply this temperature locally by touching the animal in the region to be tested with a sharply bent glass tube kept at the required temperature by a rapid flow of hot water through it. The bent tube thus heated was applied successively, but at considerable intervals, to the anterior end, middle, and tail of several animals, and their reactions recorded. As a check on this method the bent tube filled with water at 31° C. was also applied to the animals, with the outcome that the mechanical stimulation was found to be so considerable that the results dependent upon temperature could not be rightly judged, and the method was therefore necessarily abandoned.

I next tried running a gentle stream of warm sea water on different parts of the lancelet's body while it was resting in a dish of sea water at 31° C., and I checked this method by using the same strength of stream, but at the normal temperature. This procedure proved much more satisfactory than the use of the bent tube, for the current of water at the normal temperature seldom, if ever, gave rise to a response, while that at 39° C. very generally did.

When the heated current was applied to the anterior end of a lancelet, the animal very usually swam immediately backward a short distance. When it was applied to the tail, the animal often moved forward. When it was applied to the middle of the body, the reaction never was locomotor, but only a slight bending or jerking of the body, and even this was apparent in only about one out of every ten trials.

The reactions of amphioxus on being immersed in warm water or touched by a current of warm water follow so quickly on the application of the stimulus that I am convinced that stimulation takes place on the surface of the animal, for there was scarcely time for the heat to reach by conduction any relatively deep-lying part. I therefore conclude that heat is a sensory stimulus for amphioxus, and that it is very probably effective for the whole outer surface of the animal, the head being most sensitive to it, the tail less, and the middle portion of the body least.

In a second series of tests, water cooler than 31° C. was used with which to stimulate the amphioxus. When animals were transferred from water at 31° C. to water at 25° C., they swam about with

more energy than at the normal temperature. Finally they dropped quietly to the bottom.

At 20° C, they swam very energetically and near the top of the water, but finally dropped to the bottom; subsequently, on being touched with a rod, they swam, but not so energetically as at the normal temperature.

At 15° C. they swam vigorously, but soon dropped to the bottom.

At 10° C. they passed into the water without swimming, dropped to the bottom, and remained quietly there.

At 5° C. they behaved as at 10° C. After remaining on the bottom at 5° C. for five minutes, they were removed to water of ordinary temperature, where their reactions seemed to be entirely normal.

Five active amphioxus were then dropped into water at 4° C., and after half an hour they were tested and all found to be dead. The temperature of the water at the end of half an hour had fallen to 2.5° C. This experiment was several times repeated, and always with the result that death followed exposure to extreme cold for half an hour or so.

Cold water from 25° C. to 15° C. is certainly stimulating to amphioxus. At 10° C. and lower no response is given, but death may intervene, particularly at lower temperatures, from unknown causes.

All attempts at local stimulation with cold water were entirely unsuccessful. Water at 15° C., when applied as a current to the anterior end, tail, or trunk, was without effect, though, as already mentioned, immersion in water at this temperature called forth vigorous swimming. A current of water at 2° C., when applied locally to the anterior end, tail, or trunk, gave rise, as might have been expected, to no reaction.

The reactions to cold water, when they occurred, were quite as quick as those to warm water, and must therefore have been the result of a very superficial stimulation; but whether this was a stimulation of the whole outer surface, or of a special part of it, or of some special region like the entrance to the mouth, I am unable to say.

The fact that amphioxus swims away from any source of considerable heat places it among negatively thermotropic animals. That it can be stimulated to active, non-directive swimming by both heat and cold shows it to be thermokinetic. That it should be stimulated by cold, but not influenced in a directive way by this stimulus as it is by heat, favors the view that it possesses, like some higher vertebrates, separate receptors for heat and for cold.

## 4. MECHANICAL STIMULATION.

As has been pointed out already, the apparently great sensitiveness of amphioxus to light is really sensitiveness to mechanical stimulation, a form of sensitiveness long ago remarked by Merkel ('80, p. 7), who observed that a vigorous amphioxus would respond by very active locomotion to the lightest touch of the forceps.

To test the reactions of amphioxus to mechanical stimulation I first used a course pig-bristle mounted so that the rounded end could be brought into contact with any part of the animal's exterior. When the anterior end of an amphioxus resting in a shallow dish of sea water was touched even lightly with the bristle, the animal usually sprang backward, though occasionally forward. The backward spring was often accompanied by a somersault-like movement, whereby the animal became turned end for end. When the stimulus was applied to the posterior part of the body, the result was almost invariably a forward leap. This portion of the body, though sensitive, was not so much so as the anterior end. The middle of the body was much less sensitive than either of the ends, and when the tip of the bristle was applied to it, there was often no reaction. When, however, a reaction did occur, it was almost always a backward leap.

In general the reactions of amphioxus to mechanical stimulation resemble in essential respects their reactions to light, showing that the anterior end of the animal is most sensitive to such stimuli, the posterior end less so, and the middle of the body least, and that backward locomotion usually results from stimuli applied at the anterior end or the middle, and forward locomotion from stimuli at the posterior end.

By means of local stimulation the sensitiveness of different portions of the body could be roughly determined. At the anterior end, though the rostrum can be stimulated, the most sensitive parts are the oral hood and the buccal cirri. When any of these parts is touched, backward locomotion almost invariably follows. If the hood, but especially the cirri, are touched only very lightly, they close and open with a sudden movement not unlike winking. In resting animals this is often carried out in what seems to be a spontaneous manner, but close inspection shows that it is dependent upon the accumulation on the cirri of debris from the current of water usually passing in at the anterior end. When the cirri become fairly covered with minute particles of coral sand, etc., this winking movement loosens these particles, and at the same time vigorously expels the water from just within the anterior opening of the animal, and thus removes the ac-

cumulated debris. This reaction is doubtless dependent upon the mechanical stimulation caused by the particles of sand, etc., on the cirri, for, as already stated, the momentary contact of the end of the bristle with the cirri will call it forth.

The great sensitiveness of the anterior end of amphioxus, which has already been noticed by Krause (38, p. 146), is resident chiefly in the outer surface of the oral hood. This part of the animal is easily stimulated by contact with any moving body and is the region especially concerned with the reception of stimuli when, through the movements of a few individuals, a whole assembly is set in violent commotion. It is also probable that this part is especially stimulated when an amphioxus, almost buried in sand, is made to draw back under the sand by directing a fine stream of water on the exposed anterior end.

In the middle-trunk region the firm dorsal and lateral walls, and even the delicate ventral one, are relatively insensitive to mechanical stimulation.

The whole of the caudal region is more sensitive to mechanical stimuli than the trunk region, but less so than the anterior end. The surface about the atrial pore is especially sensitive to touch, and a stimulation of this region not only results often in forward locomotion, but also in a wave of contraction that passes anteriorly from the atrial opening over perhaps half the length of the thin ventral atrial wall.

As amphioxus is so easily stimulated by gross mechanical disturbances, it is not surprising to find that it will respond to such delicate mechanical stimuli as sound waves. If a glass vessel that contains resting amphioxus partly buried in the sand is gently tapped on the side, the animals, as Rice ('80, p. 8) long ago observed, usually withdraw temporarily below the sand, or at least move their cirri in a way that resembles winking. That this is not due to the vibration of particles of sand against their bodies is seen from the fact that at least the reaction of the cirri can be called forth from animals that are resting on a bed of cotton wool in a glass vessel of sea water when the walls of the vessel are tapped. Another common form of response to sound vibrations, often seen under the conditions just mentioned, is a wave-like contraction of the atrial membrane. This membrane in fact is so placed that it may be especially open to stimulation by sound waves, for it is suspended between the atrial cavity and the outer space, both of which are filled with sea water.

It is very probable that all these reactions to sound depend upon the stimulation of some part of the tactile mechanism, for in the first place amphioxus has no special organ that can serve it as an ear (Stieda, '73, p. 52), and secondly, many sound vibrations can be sensed through our tactile organs as well as our ears.

That mechanical stimulation serves as a basis for thigmotropic, geotropic, and even rheotropic reactions cannot be doubted, though Lyon (:05) has shown that rheotropism in certain fishes depends more upon sight than upon touch. All three kinds of reactions are shown by amphioxus.

The thigmotropism of amphioxus is evident from the following experiments. Ten amphioxus were liberated in a flat-bottomed glass aquarium containing a depth of 10 centimeters of sea water and five centimeters of coral sand. After half an hour all the animals had buried themselves in the sand, and after an hour and a half seven of them had come to rest with their anterior ends a little above the level of the sand, their usual position (p. 426). That these reactions were not the result of the light that fell into the dish from above is seen from the fact that similar reactions were obtained from animals that were liberated in a covered glass dish of sea water containing a layer of sand between one and two centimeters thick and illuminated by a mirror from below only. Under these circumstances the amphioxus came to rest in the sand, but in such positions that in many cases their bodies were exposed to light through the glass bottom of the dish, though their anterior ends projected into the darkness above the sand. Thus it is evident that they did not enter the sand to escape the light. Moreover, amphioxus will rest quietly, much as when it is in sand, provided all but its anterior end is covered with small fragments of glass. Through this covering the light may pass to the animal, and apparently this does not disturb it, for its quiescence seems to depend merely upon the contact of its body with the particles of glass. I therefore believe that amphioxus is thigmotropic.

The movements by which amphioxus buries itself are not without interest. As a rule the animal dropped passively through the sea water to the sand below. When it came in contact with the sand, it sometimes gave a sudden spring and disappeared below the surface. More frequently, however, it straightened out upon the sand, as noted by Müller ('44, p. 84) and by Willey ('94, p. 10), and later, particularly if it was moved by a current, it would arch and disappear below the surface, as described by Rice ('80, p. 8). Its disappearance into the sand was so quickly accomplished that it was impossible for me to ascertain by direct observation whether the animal entered the sand with the anterior end first or the tail first. Steiner ('86, p. 497) maintains that the anterior end of the animal enters the sand first, and that it may continue to burrow through the sand till this end emerges. He

further asserts that the animals are incapable of burrowing with the Müller ('41, p. 399), however, in his description of the animal's habits implies that it enters the sand tail first, and often burrows only far enough to cover the main portion of the trunk, leaving the anterior end exposed. I attempted to ascertain the truth of the matter by carefully uncovering animals that had buried themselves, thus determining by direct inspection which end had probably entered the sand first. I also noted in instances where the animal had failed to cover itself completely which end was left exposed. These instances were more conclusive than those of completely covered animals, for in these cases there was no chance for an unobserved reversal of ends as might occur where the animals were for a short time out of sight. the great majority of these cases the animals had evidently entered the sand tail first, though there were some instances, especially among the imperfectly covered ones, in which it was clear that they had entered with the anterior end first. Other evidence on this question was derived from animals on which a slight operation had been performed. Amphioxus from which a part of the tail had been removed entered the sand only after many trials, whereas others whose rostrum had been cut off but whose tail was intact seemed to have no difficulty in making their way into the sand. These observations are in agreement with what was noticed in animals that had partly or completely buried themselves, and I am therefore convinced, notwithstanding Steiner's statement to the contrary, that amphioxus usually enters the sand tail foremost.

In one respect the amphioxus buried in the sand were very different from those lying freely on the surface. The free individuals were usually very straight, as though held in form by the stiffness of the not-ochord. The buried individuals, on the other hand, had when in the sand a very tortuous outline, as though they had crowded their way in between the coarse pieces of shell and coral. Such individuals immediately became straight on being released from the sand.

Rheotropism, though present, is not a prominent feature in the reactions of amphioxus. In the inlet at the small landing pier in front of Hotel Frascati large schools of small fish could be seen definitely oriented in reference to the swift current. These schools maintained a more or less constant position by swimming against the current about as rapidly as the current would have carried them in the opposite direction. When living amphioxus were dropped into these schools, they drifted among the small fish on the way to the bottom without as a rule the least locomotor movement, and, when they did move, they never showed any tendency to orient to the current. Moreover, when

they were placed in a floating aquarium the sides of which were of netting so as to permit a strong current of sea water to pass through it, they either drifted to the far end of the aquarium or swam irregularly about and without reference to the current, though a few small fish that were caught and put into the aquarium swam against the current with precision.

These observations are in agreement with what Lyon (:05) found as to the rheotropism of certain fishes, namely, that in large general currents their orientation is dependent not upon the direct stimulus of the current, but upon the possession of a visual organ capable of forming an image whereby they could fix their position in reference to motionless objects on the banks and in the bed of the stream. Since amphioxus does not possess visual organs of such a character, orientation under these circumstances is not to be expected.

If, however, an amphioxus is put into a large cylindrical vessel filled with sea water and the water is made to whirl in it, the animal is quickly stimulated to swimming and swims vigorously against the current. After a short period of active swimming, in which the animal will often progress more rapidly than the current moves in the opposite direction, it will drop to the bottom as though exhausted and be carried round and round by the water. It was evident from the movements of the animal that the stimuli to its locomotion were the momentary contacts with the inner sides of the vessel next which it was often swept and in all probability the varying rates of those parts of the current that touched the sides of the animal. To such an irregular current amphioxus undoubtedly reacts, i. e., under these circumstances it is rheotropic.

Amphioxus can also be shown to be slightly geotropic. This feature does not appear in its swimming, for though Steiner ('86, p. 498; '88, p. 43) affirms that the whole animal, or even a quarter of it, will swim with full equilibrium, and is so quoted by Ayers ('92, p. 318) and by Sherrington ('99, p. 1276), my own observations agree with the statements of Rice ('80, p. 8) and of Willey ('94, p. 10), that in swimming amphioxus may move with any side uppermost and may continually change that side. This change of attitude during locomotion was so constant a phenomenon among the many amphioxus that I watched that there is not the least question in my mind that this animal during locomotion assumes no uniform position in reference to gravity.

In its resting state, however, amphioxus shows some slight response to gravity. As it lies on the sand it may rest for considerable periods of time with any side uppermost, but after it has burrowed and come to rest near the surface of the sand, it usually lies, as Rice (30, p. 8)

and Hesse ('98', p. 459) have noted, with the ventral side uppermost and always with the anterior end higher than the posterior. relation of the two ends might be supposed to be due to the need of having the anterior end in clear water, and therefore to be a reaction to the water and sand in the surroundings and not directly to gravity, but that this assumption is false is seen from the following experiments. If several amphioxus are placed in a closed box made of coarse wire gauze and filled with sand and the whole immersed in sea water, in a few hours they will be found at the top of the sand with their anterior ends projecting into the sea water. If now the box is cautiously inverted, some of the animals will keep their original positions, and thus their anterior ends will project from the under side of the box into the adjacent sea water; but they will remain here only a short time, for sooner or later they will make their way upward through the sand to the top. In a similar way if, after they have come to rest at the top, the box is rotated through a quadrant so that their anterior ends project sidewise into the sea water, they will again desert this position and move to the top. Further, if in a funnel whose stem has been broken off short an amphioxus is buried in sand in such a way that its anterior end projects downward out of the small end of the funnel into the sea water, it will leave this lower end and make its way upward through the sand to the top, even if, in doing so, it emerges on sand above the level of the water. It is therefore evident that amphioxus will come to rest in the sand only when its anterior end is above its posterior one, and, from the conditions under which this occurs, such responses seem to be strictly geotropic.

# 5. CHEMICAL STIMULATION.

The chemical sense of amphioxus, as remarked by Nagel ('94b, p. 192), is not unlike that of a worm in that its seat is the whole outer surface of the animal and not simply the region around the mouth. This sense is doubtless serviceable chiefly as a means toward escape from unfavorable chemical surroundings and probably has little or nothing to do with the direct feeding habits of the animal. As is well known, amphioxus does not seek its food, but takes what is brought to it in water currents, selecting from this supply only in the crudest fashion, if in fact it can be said to select at all. Nagel ('94b, p. 58) has shown that the outer surface of amphioxus is sensitive to chloroform, etc., and declares that, notwithstanding the presence of the so-called olfactory pit near the anterior end, one part of the animal's body is about as sensitive to chemical stimulation as another, though the tail may possibly be more sensitive than any other portion.

In testing amphioxus for chemical responses I used solutions of sour, sweet, bitter, and alkaline substances, as well as solutions of certain oils and other materials. All these solutions were made up in sea water, and, where the strength is expressed as parts of a molecular solution, sea water was used as a basis for this mixture instead of distilled water.

For a sour substance I used nitric acid. If a pipette full of sea water is discharged gently on the side of a resting amphioxus, there is usually no reaction. On animals thus previously tested a few drops of a  $\frac{m}{10}$  solution of nitric acid were discharged successively on the anterior end, on the middle, and on the posterior end. In all these trials vigorous locomotion was induced; backward when the region of application was the anterior end or the middle, and forward when it was the posterior end. When a  $\frac{m}{100}$  solution was applied to the anterior end or to the tail, the characteristic reactions were obtained, but there was usually no reaction when this solution was applied to the middle of the animal. A  $\frac{m}{1000}$  solution called forth no reaction when applied to the middle or the tail, but only when applied to the anterior end. A  $\frac{m}{1000}$  solution called forth no reactions at all. Hence to solutions of nitric acid the anterior end is most sensitive, the tail next, and the middle least.

A more detailed study of the anterior end showed the following conditions. In an animal that in its normal state responded when this end was stimulated by a  $\frac{m}{500}$  solution of nitric acid, the removal of the rostrum and the olfactory pit made no observable difference in its responses, thus confirming Nagel's statement ('94b, p. 192) that the olfactory pit is not essential to the special chemical sensitiveness of the anterior end. This pit, which was first described by Kölliker ('43) and was believed by him to be olfactory in function, was found in living animals to be lined with ciliated epithelium, by the movement of which particles of carmine were carried into it from its posterior edge and discharged from it anteriorly. Cutting off also the buccal cirri left the animal still receptive to a  $\frac{m}{500}$  solution. When, however, enough of the anterior end was removed to take away the velar tentacles, what remained could be stimulated only by a  $\frac{m}{100}$  or a stronger solution of nitric acid. The high degree of sensitiveness of the anterior end is therefore dependent upon parts not farther posterior than the velar tentacles. Since these tentacles and the buccal cirri are abundantly supplied with groups of sense cells (Willey, '94, p. 20), it is not impossible that the great sensitiveness of the anterior end is due to these groups of cells; but to this question I can give no conclusive answer.

To make an alkaline solution, one per cent of potassic hydrate was added to sea water, with the result that a somewhat milky precipitate was formed. The filtrate from this mixture had a strongly alkaline taste, but it did not call forth any response when it was applied either to the tail or to the middle of amphioxus. At the anterior end it caused the animal to dart backward vigorously.

For a bitter material pieric acid was used. About a  $\frac{m}{50}$  solution is very near saturation in sea water. To this solution, when applied to the tail, middle, and anterior end, amphioxus reacted with characteristic locomotion. All three regions were also stimulated by a  $\frac{m}{250}$  solution, but locomotion usually did not result. At  $\frac{m}{1250}$  occasional slight reactions were obtained, but only when the solution was applied to the anterior end, the tail and middle being apparently insensitive to this strength.

When a ten per cent solution of cane sugar in sea water was discharged freely over the anterior end, the middle, or the tail of amphioxus, no reaction of any kind was given.

No reactions were observed when the surface of the animal was bathed with sea water containing the following substances in solution: ether, chloroform, turpentine, oil of bergamot, and oil of rosemary. However, when any of these materials in a pure state was applied directly to the skin of amphioxus, a vigorous locomotor response was elicited, as Nagel ('94b, p. 58) had previously found for chloroform and oil of rosemary.

A one per cent solution of alcohol in sea water called forth no response when applied to the anterior end, the middle, or the tail of amphioxus. A five per cent solution stimulated the anterior end and tail but not the middle, and a ten per cent solution stimulated all three parts.

Not only are many chemical solutions stimulating to amphioxus, but fresh water is likewise. When animals were dropped into sea water to which had been added one-fourth fresh water, the animals were observed to swim for a time more vigorously than in pure sea water. When the sea water was diluted by an equal volume or more of fresh water, the amphioxus swam most vigorously, and in very dilute sea water or in fresh water they quickly died, as already observed by Bert ('69, p. 21) and by Johnston (:05, p. 115). These various mixtures were also locally stimulating. The mixture of one-fourth fresh water and three-fourths sea water induced a slight backward movement when applied to the anterior end, but apparently stimulated no other part of the body. All mixtures containing more than one-fourth fresh water stimulated both the anterior end and the

tail, but not even pure fresh water stimulated the middle of the animal. When any of these stimulating mixtures were applied to the head, the animal swam backward; when they were applied to the tail, the locomotion was forward.

These experiments show that the surface of amphioxus is stimulated by solutions of nitric acid (sour), potassic hydrate (alkaline), picric acid (bitter), and alcohol, and by strong ether, chloroform, turpentine, etc. It is also stimulated by sea water diluted with fresh water, a mixture of which may prove fatal. Such stimuli were most effective at the anterior end of the animal, less so at the tail, and least of all at the middle, and the reactions were always such as to enable the animal to avoid the stimulus. So far as these tests go, amphioxus may be said to be uniformly negatively chemotropic.

# 6. Interrelation of Sensory Mechanisms in Amphioxus.

The distribution of sensitiveness of amphioxus to the stimuli discussed in the preceding sections follows a very simple plan. To light, heat, mechanical and chemical stimuli, the anterior portion of amphioxus is more sensitive than the tail, and the tail is more sensitive than the middle region of the trunk. A more accurate comparison of the distribution of sensitiveness has shown that a response to light cannot be elicited when the most anterior part of the body is illuminated, though this region is very easily stimulated by either heat, mechanical or chemical means. This fact and the agreement of the degrees of sensitiveness to light with the numbers of eye-cups in different parts of the nerve-tube have been given a reason for the conclusion that the light receptors in amphioxus are the eye-cups themselves and not the nerve terminals in the skin. Since the receptors for heat, mechanical and chemical stimuli, lie in the skin, they must be distinct from the photoreceptors. Further evidence of this separateness is, however, seen in results obtained by exhaustion. If the tail of an amphioxus is stimulated by concentrated sunlight ten or twelve times, the animal will reach a state in which it no longer responds to the illumination. While in this state it will react, however, with great certainty when its tail is stimulated by water as 37°C., by contact with a camel's-hair brush, or by a " solution of nitric acid. Thus from the standpoint of exhaustion the receptors for light can be shown to be physiologically distinct from those for the other stimuli.

The extent to which separate receptors in the skin might be distinguished for the several effective stimuli cannot be judged by the distribution of sensitiveness for these stimuli, because, so far as I could make

out, this distribution was the same for all such stimuli. Evidence on this point was to be had, however, from the following experiments on exhaustion. After about twenty applications of a m solution of nitric acid to the tail of an amphioxus, the animal usually ceased to respond to this stimulus. But on testing the same part of its body with water at 37° C. or with contact from a camel's-hair brush, it was found to be immediately responsive. In a similar way about thirty vigorous strokes of a camel's-hair brush were needed on the tail of an amphioxus before it ceased to react to this form of stimulation, whereupon it was found still to be sensitive to water at 37° C. and to a solution of nitric acid. Finally after an animal had ceased to react to water at 37 C. it was still sensitive to contact with the brush and to acid. Thus, notwithstanding the fact that the distribution of sensitiveness for these several stimuli is such as to leave the question as to separate receptors unsettled, exhaustion shows very conclusively that their operations are physiologically distinct (Parker, :07, p. 724), and as there is no evidence that they may not be represented by separate terminal organs in the skin, I believe that such organs are probably present. To what extent a further discrimination might be possible, as, for instance, the separation of terminal organs for cold and for heat, or for the different kinds of chemical stimuli, cannot be stated, for no experiments in this direction were undertaken.

To all the forms of effective stimuli that I employed, amphioxus responded in but one way, namely, with such movements as would remove it as directly as possible from the presence of the stimulus. When the stimulus was applied to the anterior end or to the middle trunk region, the animal moved backward, and when the application was to the tail, it moved forward. In not a single kind of stimulus did the animal move regularly toward the stimulus. This negative response, which seems to pervade the whole sensory activity of amphioxus, is the basis of its habit of retreat and characterizes much of what it does. Even feeding, which is so usually a positive operation with animals, is in amphioxus a relatively passive affair and unconnected with any seeking reactions. It therefore seems that the whole sensorv system of amphioxus is employed as the initial mechanism in removing the animal from possible danger rather than as an apparatus for leading it successfully into new territory. This feature, as Steiner ('88, p. 42) has already remarked, is perhaps the most striking peculiarity of the sensory reactions of amphioxus.

The negative response of amphioxus to stimulation is of importance in considering the question of the direction in which it swims. Rice ('80, p. 8) declares that amphioxus always swims with its anterior end

foremost and that he never saw it move with its tail in advance. Steiner ('86, p. 497; '88, p. 41) also asserts that the animal moves with the anterior end foremost. The locomotion of amphioxus is a rapid, curiously irregular wriggle, often accompanied with somersault-like movements which make it impossible to be sure at any moment whether the animal is swimming backward or forward. The results of momentary stimulation, however, show very conclusively that amphioxus can swim both backward and forward, and that the direction of swimming at the beginning of any course is dependent upon the part of the animal's body that was stimulated. But how long amphioxus keeps to one form of movement I was unable to discover. The fact that it usually buries itself in the sand tail first (p. 433) leads me to believe that, though it can swim forward, as maintained by Rice and by Steiner, it usually swims backward.

Another feature of the reactions of amphioxus is their great energy, which is quickly followed by what seems to be complete collapse. For a few moments the animal swims with the utmost vigor, and then drops down quite motionless, as though it had become entirely exhausted (Rice, '80, p. 9). That this is not exhaustion is seen from the fact that a slight stimulus will usually cause a second round of activity; but after a few such efforts, the animal becomes unresponsive to further stimulation and is doubtless temporarily exhausted.

# 7. CENTRAL NERVOUS SYSTEM AND SENSORY MECHANISMS IN AMPHIOXUS.

To what extent the uninjured central nervous system of amphioxus is essential to its sensory reactions has already been briefly alluded to in the account of this animal's reactions to light (p. 424), but now that the other classes of stimuli have been described a more extended discussion of this subject may be undertaken. Steiner ('86, p. 498: '88, p. 43), who was apparently the first to investigate the functions of the central nervous system in amphioxus, states that after an animal had been cut into two, three, or even four parts, all the parts reacted to mechanical stimulation by swimming forward, and from these observations he concluded that the central nervous system of amphioxus is a metameric structure without sufficient differentiation to allow one to divide it into brain and spinal cord. Although his description of the reactions of the pieces of amphioxus might lead one to infer that these fragments reacted exactly as the whole animal did, it is plain from his further account that such fragments were less sensitive than when they made a part of the whole animal; for he goes on to remark that, when

the sensitiveness of the fragment becomes much lowered, it is only necessary to put the piece in very dilute picric acid to call forth the characteristic locomotion again. Johnston (:05, p. 124), however, states that even a small piece of the tail of amphioxus can swim well and behaves much as the whole animal does. Nagel ('94a, p. 811; '96, p. 79) declares that both halves of an amphioxus react promptly to light, but less energetically than the whole animal does. But Danilewsky ('92) maintains that the halves react, at least to mechanical stimuli, very differently; the anterior half is quite sensitive to this form of stimulus, but the posterior half can be brought to react only with difficulty. Krause ('97, p. 514) declares that the anterior half reacts vigorously to light and the posterior half only slightly. Hesse ('98b, p. 462), however, states that after division the anterior part only trembles on being illuminated and the posterior part gives no reaction whatever.

My own observations on B. caribbaeum lead me to believe that whether reactions will be given by both halves of this amphioxus or not depends quite as much upon the nature of the stimulus as upon any other factor. To light, as already stated, I have never been able to get any response from the posterior half, though the anterior half regularly trembled whenever strong light was thrown upon it. In these respects my results agree exactly with those of Hesse, and they were, moreover, so uniform and regular that I am led to suspect the accuracy of Krause's and of Nagel's statements, at least so far as they apply to the posterior half of amphioxus. After the nerve-tube is cut, this part seems no longer able to respond to light. is due to the small number of eye-cups in this region, as Hesse believed, is not true, for, as a matter of fact, these cups are almost as numerous in the tail region as in any other part of the animal. my opinion the failure of the posterior half of amphioxus to react to light is not due to the lack of sensitiveness, but to the interruption of some centrally situated, reflex path. In the posterior half, apparently, the sensory neurones that are stimulated by light cannot transfer their impulses directly to the motor neurones of the same region, but only indirectly through the anterior part of the nerve-tube; hence when this is removed the reflex ceases. It is in this way, rather than through altered sensibility, that an explanation of this phenomenon will, I believe, be found.

To mechanical, and especially to chemical, stimuli I found both halves of amphioxus to be responsive, not, however, as Steiner describes, but rather as stated by Danilewsky, in that the anterior part was found to be quite sensitive and the posterior part slightly so. These observations suggest that the central tracts over which photic impulses pass are separate from those which transmit sensory impulses from the integumentary terminals. Since they show, further, that the anterior half of the nerve-tube is different in function from the posterior half, they are opposed to Steiner's view of a metameric nervous system with equivalent segments, and favor the opinion advanced by Ayers ('90°, p. 223) and supported by Danilewsky ('92), that the anterior end of the nerve-tube of amphioxus is already a primitive brain and the posterior portion a spinal cord.

# 8. Sensory Mechanisms in Amphioxus and their Relations to Vertebrate Sense Organs.

The conditions presented by the sensory mechanisms in amphioxus give some clue to what was probably a step in the differentiation of the sense organs in primitive vertebrates. In these forms tactile organs doubtless covered the whole exterior, as they now do the body of amphioxus and that of the higher vertebrates, but these primitive ancestors, like amphioxus, probably possessed nothing by way of differentiations of these organs. Such differentiations are represented by the lateralline organs and the ears, both of which occur in the cyclostomes and the higher vetebrates, but are wholly unrepresented in amphioxus, for the ear supposed by Peters ('77, p. 854) to have been seen in this animal is well known not to occur there. From the embryology of these organs it seems probable, as Ayers ('92) has pointed out, that specialized tactile organs gave rise to lateral-line organs, and that from certain of these lateral-line organs the ear was differentiated. This history, based upon morphological considerations, is parallel to what is known of the physiology of these parts, for the lateral-line organs are stimulated by material vibrations of low rate (Parker, :051; :03a; :03b), possibly also effective as tactile stimuli, and the ear is stimulated by material vibrations of a higher rate, such as we recognize as sound. In my opinion the stimuli for these three sets of sense organs may often overlap and the three sets of organs constitute a genetic series, in which the tactile organs are the oldest members and the ear the newest. Although the primitive functions of these parts were doubtless (1) touch, (2) reception of slow vibrations, and (3) hearing, all these parts, but especially the ear, became involved more or less in the reflexes of equilibrium. This relation, however, I believe to have been entirely a secondary one, and not in any way to represent the original function of these organs as intimated by Lee ('98); hence I have avoided any such expression as equilibration sense. Amphioxus thus represents an ancestral vertebrate with tactile organs, but without lateral-line organs or ears, and in it the equilibration reflex can be said scarcely to have developed as yet. In this respect it is like a young lobster before the statocyst has been formed (Prentiss, :01), and its powers of orientation to gravity, revealed in only a slight geotropism when at rest, are correspondingly small.

As the receptive organs for mechanical stimuli probably represent a primitive stage from which the lateral-line organs and the ears of the higher forms have developed, so the receptors for light doubtless give some idea of what served as a source for the lateral eves of vertebrates. It has already been pointed out that the only organs that are known to be light receptors in amphioxus are the eye-cups. Hesse ('98'), p. 462), however, who was most instrumental in establishing this fact, does not regard these organs as in any way the homologues of the vertebrate eye, and in this opinion he is followed by Joseph (:04, p. 25). But I must confess that to me the evidence seems to point very definitely to the conclusion already drawn by Boveri (:04, p. 411) that the sensory cell of each eye-cup is homologous to a rod- or a cone-cell. In my opinion the eye-cups of amphioxus represent a diffuse sensory material from which an eye, like the lateral eye of the vertebrate, or even a series of eyes, as suggested by Locy (97), could have developed, much as the ears of these animals have been differentiated from their lateral-line organs. The objection to this view raised by Joseph (:04, p. 24) that the photo-receptors of amphioxus do not occur in the exact region from which the lateral eyes may have arisen does not appear to me to be really serious.

The steps whereby the lateral eyes have come into existence are by no means easily retraced, and it is for this very reason that any indication such as that afforded by amphioxus is of the utmost importance. Whatever has been the exact course followed by the eye in its differentiation, two remarkable but well-recognized features have resulted; first, the retinal elements of the lateral eyes are inverted in relation to the stimulus as compared with the great majority of sense organs, and, secondly, the retina in vertebrates develops not directly from the external ectoderm, but as an outgrowth from the brain. It is rather striking that two investigators have published, apparently quite independently, essentially the same explanation of these facts. Balfour ('85, p. 508) long ago pointed out that, if we imagine that the retinal part of the lateral eye was involved in the infolding that gave rise to the central nervous organs, then the final positions of the rods and cones at the surface of the retina away from the light would be satisfactorily explained, for this surface is the morphologically external surface of the ectoderm. This explanation assumes that the eve was

functional on the exterior of the vertebrate ancestor before this animal had an infolded central nervous system, and that in the course of its differentiation it had passed as a functional eye into the deeper parts of the head and out to the surface again, a process not so difficult to understand when it is kept in mind that the bodies of many tunicates and of amphioxus are relatively transparent. Essentially the same explanation has been brought forward recently by Jelgersma (:06), who believes that the eye in its transition between its supposed place of origin in the skin and its final position in the vertebrate head is well represented by the eye of the larval tunicates. Boveri (:04) has called attention to the strong probability that the lateral eye has been derived from photoreceptors in the central nervous system, and has pointed out that the eye-cups of amphioxus are the probable source. He has not, however, attempted to trace these eye-cups back, as Jelgersma (:06, p. 393) has done, to a possible origin in the skin, but implies that they may have arisen in place.

Although I believe that the explanation first advanced by Balfour as to the origin of the lateral eyes of vertebrates has some truth in it. there are certain aspects of it which in view of the present investigations need further consideration. Its first assumption is that the skin of the ancestral vertebrate contained photoreceptors. The fact already mentioned, that the skin of some amphibians and fishes, particularly ammocoetes (Parker, : 03°, : 05°), is so supplied, would lead to the expectation that the skin of amphioxus would also contain such organs. My own studies have given no grounds for this belief, and, though I have not been able conclusively to prove the contrary, the evidence seems to favor the idea that the skin of amphioxus is not sensitive to light. As nothing is known, so far as I am aware, of the condition of the skin in this respect in tunicates, adult or young, the belief that the skin of the ancestral vertebrate contained photoreceptors must remain a pure hypothesis, and it is conceivable that the photoreceptors of the vertebrate eye may have arisen, not in the skin before the central nervous system was differentiated, as suggested by Balfour and by Jelgersma, but, as intimated by Boveri, from the cells of the central nervous system itself, in positions much as we find them now in amphioxus.

The assumption of an external origin for the vertebrate photoreceptors is helpful only in that it appears to offer an explanation of the inverted positions of the rods and cones in the vertebrate retina. But this explanation requires that from the time the photoreceptors were formed in the skin till they made a part of an organized retina, they should occupy the morphologically outermost portion of the cellular

layer in which they were imbedded and that the individual photoreceptors should be so oriented that their sensory ends would be toward the morphologically outer surface of this layer and their nervous ends away from it. In amphioxus it is true that the photoreceptors lie near the morphologically outer surface (the surface of the central canal). but their orientation is by no means constant in relation to this surface. In some the sensory ends point toward this surface, but in most such is not the case, and in a few they may even point away from this sur-It therefore seems to me obviously impossible to explain the orientation of the retinal rods and cones as transferred from the skin to the retina through a series of stages in one of which as much freedom of position is shown as among the photoreceptors of amphioxus. Nor, as Metcalf (:06, p. 528) has pointed out, is the condition more favorable in the larvae of the tunicates, for here the photoreceptor cluster in the brain is so large compared with the thickness of the cellular wall in which it is imbedded (Froriep, :06, p. 145) that its orientation is no more related to the morphologically outer surface of the wall than that of the eye-cups of amphioxus is. For these reasons I believe that the inversion of the vertebrate rods and cones in relation to the light is not due to their origin from definitely oriented external photoreceptors, and since there is no positive evidence of the existence of these receptors in the skins of animals that may fairly represent ancestors of the vertebrates, it seems to me that we are not warranted in assuming their presence at all. I therefore agree with Boveri in believing that the photoreceptors of vertebrates have arisen in the central nervous system and not in the skin, as assumed by Balfour and by Jelgersma.

If the unusual position and orientation of the rods and cones in the vertebrate retina are not due to the origin of these bodies from external photoreceptors, how then are these peculiarities to be accounted for? The position of the photoreceptor near the central canal is due in my opinion to the method of growth of the nerve-tube, for the epithelium surrounding the central canal is the source of the various cells in the wall of the tube. When, therefore, a new type of cell, like the photoreceptor, appears, it would be natural to expect it to arise from this undifferentiated material, and, in my opinion, the photoreceptors of amphioxus and of the tunicate larvae are in their position of origin. This position is retained by their derivatives the rod- and cone-cells.

The very exact orientation of the rods and cones involves factors quite different from those that govern their general position. The eye-cups of amphioxus show only a very slight degree of orientation, but so far as this goes, it is correlated with habit, in that the majority

of the eye-cups are directed ventrally and the animal usually rests in the sand obliquely with the ventral side uppermost. Thus the majority of the eye-cups are in a position to receive effective stimulation. If we imagine the body of amphioxus to be increased in muscular strength, etc., whereby it would approach more nearly the condition in the fishes and would consequently add much to its thickness, it follows that the posterior portion would become less transparent and the photoreceptors of the anterior end would be the only ones left in position for effective stimulation. With the development of the mouth cavity, the gills, etc., the source of light for the anterior photoreceptors would become chiefly lateral and dorsal, and their orientation would doubtless conform to this plan of illumination. If in accordance with this scheme each eye-cup assumed the best possible orientation, it would lie with its open end directed laterally and perhaps somewhat dorsally, i. e., the contained sense cell would be oriented with its sensory end away from the light and its nervous end towards this stimulus. With the disappearance of the surrounding pigment cells as the cluster of photoreceptors became a single retina, these elements would be oriented as the rods and cones are. It is in this way, I believe, that the rods and cones of the vertebrate eve have become inverted, rather than that the inversion is inherited from a condition on the external surface of the body.

Not only may the rod- and cone-cells be thus oriented at the beginning, but it seems to me that their subsequent relations to the surrounding parts tend to keep them so. The chief factor in this respect is the supply of materials necessary for their activity. Directed as they are away from the central dioptric part of the eye, their sensory ends, which are the parts most quickly exhausted by activity, are turned toward the chief blood-supply, the choroid layer of the eye, and are. therefore, in a most advantageous position to receive new materials for metabolism. That important substances reach them from this side is seen in the fact, well attested by experiment, that if the retinal pigment layer is removed from a live retina, the regeneration of the visual purple in the rods is much retarded, if not completely stopped, though simply placing the layer back again upon the retina will cause this process to be resumed. Thus the inverted position of the rod- and cone-cells is the one best adapted to keep their most easily exhausted parts nearest the supply of materials necessary for their activities and still hold them open to access to light. This factor is doubtless one that has tended to retain the rod- and cone-cells in their inverted positions.

The condition of light receptors in amphioxus lends no support to

such views of the origin of the lateral eyes of vertebrates as have been advanced by Sharp ('85), Burckhardt (:02), and others, according to which the lens is regarded as having been derived from the primitive retina, now replaced by a photoreceptive differentiation of a deeper ganglionic part. I agree with Boveri in looking upon the eye-cups of amphioxus and, I may also add, the corresponding elements of the tunicate eye as the forerunners of the vertebrate retina, and, though I was at first inclined to ascribe to these a direct origin from the external skin, I now believe that we at least have no good reason for this assumption.

The chemical sense is the only one in amphioxus that seems to possess a well-marked special organ, the so-called olfactory pit, and yet for this organ both Nagel's experiments and mine gave no signs of sensitiveness other than that which characterizes the skin of the anterior end. Notwithstanding this negative evidence, the morphological relations of this pit are such that I believe it is very probably the homologue of the olfactory organ of the higher vertebrates. a special function has not been discovered for the olfactory pit in amphioxus is perhaps not surprising when it is remembered that no direct physiological evidence whatsoever is at hand bearing on the function of the olfactory organs of fishes. That these organs are undoubtedly of great significance in the life of a fish is attested by the extent of their surfaces and by the size of the connected parts of the brain, and yet, so far as the habits of fishes are concerned, we have no conclusive evidence as to their real uses.

The outer surface of amphioxus is sensitive to a variety of substances, such as nitric acid, picric acid, alcohol, etc., and to all these substances the animal responds by withdrawing. Nothing could be discovered about its reactions that could lead to the belief that the chemical sense was connected with feeding. This sensitiveness was found in amphioxus to be dependent, not upon nerves from the region of the mouth that had invaded the outer skin, as Herrick (:03) has shown for many fishes, but upon the segmental nerves of the region stimulated, for the posterior third of an amphioxus will react, like the whole animal, to effective chemical stimuli. The chemical sense of amphioxus is, then, not especially associated with its mouth or its feeding habits, but is a general integumentary sense, the function of which seems to be to help the animal to escape an unfavorable chemical environment. Apparently this is the primitive function of the chemical sense as it is met with in the skins of many animals, and this unspecialized sense has afforded a basis from which in the region of the mouth the specialized senses of smell and taste (both of which are

chiefly concerned with food discrimination) have been differentiated. This unspecialized chemical sense has been retained in the skin of the frog and other amphibians and in the irritable mucous surfaces of the higher vertebrates, but its chief representatives in the higher forms are its derivatives, the senses of taste and of smell. Of these, amphioxus possibly possesses the sense of smell.

Amphioxus may, therefore, be said to be an animal that possesses in potentia at least the sense organs of the vertebrates. Its outer surface is provided with tactile organs, but it does not possess the derivatives of these, the lateral-line organs and the ear. Its outer surface also contains undifferentiated chemical sense organs, but it cannot be said to have a sense of taste, and the only evidence of a sense of smell is morphological. Its outer surface, like that of the higher vertebrates, contains temperature organs. Amphioxus also has in the walls of its nerve-tube photoreceptors, which may well be the forerunners of the rod- and cone-cells of the vertebrate retina. It is thus an animal of fundamental importance for the understanding of the vertebrate sense organs.

# 9. Summary.

- 1. Amphioxus is only very slightly sensitive to light.
- 2. It responds to a rapid increase of light, but not to a rapid decrease.
- 3. The only known photoreceptors in amphioxus are the eye-cups in the wall of the nerve-tube.
  - 4. Amphioxus is photokinetic and negatively phototropic.
- 5. Amphioxus is stimulated by water warmer than that in which it lives (31° C.) and is killed in water at 40° C. or higher.
- 6. It is also stimulated by water colder than 31° C. and is killed by lengthy exposure to water of 4° C. or lower.
  - 7. It is thermokinetic and negatively thermotropic.
- 8. The outer surface of amphioxus, especially the oral hood and the tentacular cirri, is sensitive to mechanical stimuli.
  - 9. Amphioxus is also sensitive to sound vibrations.
  - 10. It is thigmotropic, and slightly rheotropic and geotropic.
- 11. The outer surface of amphioxus is sensitive to solutions of nitric acid, potassic hydrate, picric acid, alcohol, and to strong ether, chloroform, turpentine, oil of bergamot, and oil of rosemary, but not to solutions of sugar. It is also stimulated by diluted sea water and by fresh water.
  - 12. Amphioxus is negatively chemotropic.

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- 13. The photoreceptors in amphioxus are anatomically distinct from the receptors for thermal, mechanical, and chemical stimuli, and these three are at least physiologically distinct one from another.
- 14. To all stimuli that induce locomotion amphioxus responds by forward movements when the stimuli are applied to the tail, and by backward movements when they are applied to the middle or to the anterior end.
- 15. Amphioxus generally buries itself tail first, and in all probability usually swims tail first, though it may reverse both processes.
- 16. When amphioxus is cut in two, both halves lose much in sensitiveness, the posterior proportionally much more than the anterior. The anterior part of the nerve-tube is brain-like, the posterior part cord-like.
- 17. The skin of amphioxus contains tactile organs, but amphioxus possesses no derived organs such as lateral-line organs and ears.
- 18. The photoreceptors of amphioxus are the eye-cups of the nervetube, and these probably represent the elements from which the rod-and cone-cells of the lateral eyes of vertebrates have been derived.
- 19. The rod- and cone-cells of the vertebrate retina are inverted, not because they have retained a morphological position dependent upon an external origin, but because of their orientation acquired as effective eye-cups in the nerve-tube of a primitive vertebrate.
- 20. The chemical sense organs of amphioxus are located in the skin and are chiefly important as organs for testing the character of the chemical environment rather than for the selection of food. From these undifferentiated chemical sense organs have probably been derived the organs of taste and smell, of which the former are apparrently not present in amphioxus and the latter may be represented by the so-called olfactory pit.

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# ON DELAYS BEFORE ἀναγνωρίσεις ΙΝ GREEK TRAGEDY.

BY WILLIAM P. DICKEY.

chapter xvi. Such portions of this chapter as serve my purpose will be mentioned later.

My study of the above-mentioned passages of Aristotle has naturally referred me to recognition scenes in the Odyssey, from which it appears that such scenes are as old as Greek literature. It is interesting to note that the Homeric recognition scenes are comparatively simple,4 but none the less effective and in keeping with the general character of the epic. A brief examination of these scenes follows. At the beginning of the fourteenth book of the Odyssey Odvsseus returns to Ithaca, and, in the guise of a beggar, presents himself at the hut of Eumaeus, the swineherd, where he receives a warm reception. One might expect that Odysseus, overjoyed by his safe return, would disclose his identity at once, but not so; even an epic poet could show ingenuity in delaying recognition scenes so as to make them occur where they suited his purpose best. In this particular case it was necessary to interpose a delay until Telemachus could return from Sparta, and incidentally the poet had an opportunity to pit Eumaeus and Odysseus against each other as story-tellers, whereby the latter became acquainted with the general situation of his household affairs. Finally Telemachus appears at the hut of Eumaeus at the beginning of Book XVI, yet there is no spontaneous recognition between father and son; but after Eumaeus has gone to the palace to inform Penelope of the arrival of Telemachus, Athena (1725) transforms Odysseus, the beggar, into Odysseus, the prince, who (188) declares to his startled son ἀλλὰ πατὴρ τεός εἰμι. In spite of this divine manifestation, Telemachus doubts, and delays his final acquiescence until 214,6 after Odysseus has explained the transformation. Therefore, since we cannot regard this recognition as complete until 214, and inasmuch as the evidence is all in at 188, and what follows to 213 is a mere explanation, or résumé, of the real evidence. I must consider the intervening verses a conscious delay which I shall designate as secondary, as distinguished from that more general and longer delay (in this case from the beginning of Book XVI to verse 172), which may properly be called primary. Let us take another case and see if we can detect a similar delay.

<sup>&</sup>lt;sup>4</sup> I am inclined to believe, however, that the recognition seenes show some development, though it is not my purpose now to discuss the relative chronology of books of the Odyssey on the basis of recognition seenes. Throughout this paper my references to 'Homer' are in the generic sense.

 <sup>5</sup> η, καὶ χρυσείη βάβδφ ἐπεμάσσατ' 'Αθήνη. (I quote Cauer's text of the Odyssey.)
 6 Od. XVI, 213-214: Τηλέμαχος δέ | ἀμφιχυθεὶς πατέρ' ἐσθλὸν ὀδύρετο δάκρυα λείβων.

In Book XIX, 53ff.<sup>7</sup> we find Odysseus, in response to her request, before Penelope ready for the interview in which he hears her story of her trials with the suitors, and in which he, upon request, discloses his fictitious lineage, adding a charming account of himself as host of Odysseus in Crete, and closing with the utterance of his belief that Odysseus will return. However much Odysseus might naturally have desired a recognition at this point, the poet would not allow it. The 'primary' delay in this case was to continue to Book XXIII, about which I shall have something to say later. To continue with Book XIX, we see that Odysseus so endeared himself to Penelope by his specious stories that she gave an order that he be well entertained. Then follows the bath scene and the recognition of Odysseus by his old nurse, Eurycleia. It will be observed that this recognition is preceded by a 'primary' delay, and so managed that the scar on the foot of Odysseus is to be recognized by Eurycleia only, who is made to keep the secret and become an aid to her master in executing his plans. The general order of Penelope to her maids to wash the feet of Odysseus and prepare his bed is met by his objection and his suggestion that some aged,8 sober-minded woman, who had borne as many sorrows as himself, might touch his feet, etc. The 'primary' delay in this case extends from 317 (where Penelope says to her maids, ἀλλά μιν, άμφίπολοι, ἀπονίψατε, κάτθετε δ' εὐνήν) to 376, where Eurycleia, after a touching reminiscence of her master, says: τῶ σε πόδας νίψω, ἄμα τ' αὐτης Πηνελοπείης | καὶ σέθεν είνεκ', ἐπεί μοι ὀρώρεται ἔνδοθι θυμὸς | κήδεσιν, άλλ' ἄγε νῦν ξυνίει ἔπος, ὅττι κεν εἴπω : | πολλοὶ δὴ ξεῖνοι ταλαπείριοι ἐνθάδ' ϊκοντο, | άλλ' ου πώ τινα φημὶ ἐοικότα ὧδε ἰδέσθαι, | ὡς σὺ δέμας  $\phi \omega \nu \dot{\eta} \nu \tau \epsilon \pi \dot{\phi} \delta as \tau'$  'Οδυσηι ἔοικας 9 — almost a case of recognition έκ συλλογισμοῦ — to which Odysseus replies, ὧ γρηῦ, οὖτω φασὶν ὅσοι ίδον  $\dot{\delta}\phi\theta$ αλμοῖσιν | ήμέας ἀμφοτέρους, μάλα εἰκέλω αλλήλοιιν | ἔμμεναι, ὡς σύ περ αὐτὴ ἐπιφρονέουσ' ἀγορεύεις. Following close upon this intuition of Eurycleia occurs the statement in 392-393, αὐτίκα δ' ἔγνω | οὐλήν, κτλ. To be sure, the old nurse recognized the scar and immediately gave utterance to  $\hat{\eta}$   $\mu \dot{\alpha} \lambda'$  'Oδυσσεύς έσσι, φίλον τέκος, 11 κτλ., but, in effect, the poet's zeal for accounting for the scar really delays for the reader the completion of the recognition until 474 — a rather remarkable continuation of the 'secondary' delay, which was possible for the epic, but impossible, I take it, in a similar case, for tragedy.

A third case of recognition in the Odyssey that deserves notice is

<sup>7 ()</sup>d. XIX, 53: η δ' Τεν έκ θαλάμοιο περίφρων Πηνελόπεια κτλ.

<sup>8</sup> Vid. XIX, 346-348.

<sup>9</sup> Od. XIX, 376-381.

<sup>10</sup> Ibid. XIX, 383-385.

<sup>&</sup>lt;sup>11</sup> Ibid. XIX, 474.

found in Book XXI, 193 ff.<sup>12</sup>, where Odysseus reveals himself to Philoetius, the neatherd, and Eumaeus, the swineherd. In this case the 'primary' delay is obvious; the poet purposely delayed this scene until it suited his purpose best, which was to prove the loyalty of these servants and to secure their services for the work in hand against the suitors. Here also a 'secondary' delay occurs, though it is short <sup>13</sup> and pointed. Odysseus makes sure of their loyalty, declares himself, and produces the scar as evidence.

Again, in Book XXII, 35,14 Odysseus reveals himself to the suitors, a recognition long delayed by the poet. This recognition is momentarily expected from the time that Odysseus strung the mighty bow (XXI, 409,15 and in 412,  $\mu\nu\eta\sigma\tau\dot{\eta}\rho\sigma\iota\nu$   $\delta$ '  $\check{a}\rho$ '  $\check{a}\chi$ os  $\gamma\dot{\epsilon}\nu\dot{\epsilon}\tau$ o  $\mu\dot{\epsilon}\gamma a$ ), but the poet interposes a slight delay until Odysseus has slain Antinous. Then he declares himself to the suitors and predicts their destruction. 16

Finally, we have to consider the recognition scene between Odysseus and Penelope, which is consummated in Book XXIII. How skilfully did the poet pass by many opportunities and delay this scene until the serious business of housecleaning had been finished! 17 In the beginning of Book XXIII Eurycleia, under orders from Odysseus, goes to awake 18 Penelope and to announce that her husband is present. Here begins the 'secondary' delay, which is rather longer than in the cases noted above, the conclusive evidence beginning at 183 ω γύναι, κτλ., and concluding at 204 19 — an account of Odysseus' massive bed in his chamber fashioned about an olive shrub. It will be observed that the poet has made more of this recognition scene than any of the others. Penelope is rather obstinate and hard to convince; she will not accept the statements of the old nurse, even when she hears of the scar, — an evidence of the poet's good taste, — but must test him according to signs 20 hidden from the rest. Thereupon Odysseus convinces her by his story of the bed mentioned above. In this case it appears that Penelope reasoned thus: only Odysseus could have such knowledge

<sup>12</sup> βουκόλε καὶ σύ, συφορβέ, ἔπος τί κε μυθησαίμην κτλ.

<sup>13 193-206.</sup> 

<sup>14</sup>  $\tilde{\omega}$  κύνες, οὔ  $\mu$ ' ἔτ' ἐφάσκεθ' ὑπότροπον οἴκαδ' ἰκέσθαι κτλ.

<sup>15</sup> ΧΧΙ, 409: . . . τάνυσεν μέγα τόξον 'Οδυσσεύς.

<sup>16</sup> Ο d. ΧΧΗ, 41: νῦν ὑμῖν καὶ πᾶσιν ὀλέθρου πείρατ' ἐφῆπται.

<sup>&</sup>lt;sup>17</sup> I maintain that our poet in thus delaying this recognition scene displays no little knowledge of human nature.

<sup>18</sup> ΧΧΙΙΙ, 5 ff. : ἔγρεο, Πηνελόπεια, φίλον τέκος, ὕφρα ἴδηαι, κτλ.

<sup>19 203–204: . . .</sup>  $\lambda \epsilon \chi$ os, ἢ $\epsilon$  τις ἥδη | ἀνδρῶν ἄλλοσε θῆκε, ταμὼν ὕπο πυθμέν'  $\epsilon$ λαίης.

<sup>20</sup> Od. XXIII, 109–110 : ἔστι γὰρ ἡμῖν | σήμαθ' & δὴ καὶ νῶι κεκρυμμένα ἴδμεν ἀπ' ἄλλων.

about the bed, etc.; this man has the knowledge, therefore he is Odysseus—a clear case of ἀναγνώρισις ἐκ συλλογισμοῦ, which Aristotle 21 recognizes as second best.

Thus stand the Homeric recognition scenes that have come to my knowledge 22 - scenes comparatively simple, and yet such, I think, as show some development from the simple to the complex. In view of the foregoing study I conclude that the poet had full control over his recognitions, and did not insert them in a haphazard way, but with due regard for the purpose for which they were intended, in consequence of which his skill and ingenuity in the matter of 'primary' delays had free play; and that there is just reason for postulating 'secondary' (or shall I say prefatory?) delays which in the case of the epic are, in effect, announcements to the reader or hearer that recognitions are about to take place. Now, that 'primary' delays before recognitions in Greek tragedy are evident is likely to be conceded by all. The importance of recognition scenes in Greek tragedy must be obvious to every student of Greek literature, regardless of his knowledge of Aristotle's Poetics. That the Greek tragic poets show much variety and skill in handling such scenes, particularly in the matter of delaying them to the point where they considered them most effective in their particular plots, must be patent to any one who has read the plays in which recognition scenes occur. Therefore, in the following study of recognition scenes in Greek tragedy, what I have chosen to call 'primary 'delays I shall consider only incidentally, and shall give most of my attention to the special delays which I assume usually appear before the final act of recognition, and which, for the want of a better name, I have denominated 'secondary.'

With deep regret that I am unable to determine the nature of the many recognition scenes, which we know existed in intervening literature, <sup>23</sup> I must take a long step from the Odyssey to the Choephori of Aeschylus; and, having passed from epic to tragic poetry, I am sorely disappointed in finding extant so few of the many tragedies <sup>24</sup> that had recognition scenes — Aeschylus furnishes us a single recognition scene; Sophocles, two; Euripides, five, if we count two for the Iphigenia in Tauris.

<sup>&</sup>lt;sup>21</sup> Poetics, XVI, 12.

<sup>22</sup> It does not seem worth while to record my private consideration of that excellent recognition seems (XVII, 292 ff.) in which "Αργος was πρωταγωνιστής.

<sup>23</sup> The Νόστοι of the Trojan Cycle, the source of the Choephori, the Electras, Helen; the Οιδιπόδεια of the Theban Cycle; the 'Ορέστεια of Stesichorus, etc.

<sup>24</sup> Our knowledge of lost tragedies in which recognitions existed is too meagre to be of any value for this report.

# The Choephori of Aeschylus.

In considering the recognition scene of the Choephori I shall try to avoid any generalizations on Aeschylus's mode of dealing with recognition scenes, except to state that it seems likely that the real father of Greek tragedy probably adhered more closely to the models of his predecessors, and that his recognition scenes were simpler than those of his successors. What then is the nature of the recognition scene in the Choephori? I consider it somewhat as follows. Knowing that every form of the legend upon which this drama is built requires an ἀναγνώρισις, the audience 25 at the very outset has a prepossession that there is to be a recognition scene, and it seems safe to assume that to this the nimble-witted Greeks look forward, eager and curious to see how Aeschylus is going to handle the scene. This prepossession of the audience is reinforced by the action of Orestes in 6-7.26 πλόκαμον Ἰνάχω θρεπτήριον, | τὸν δεύτερον δὲ τόνδε πενθητήριον. this it is only a question of delay, and, in this case, the 'primary' delay continues to 165 where Electra says, νέου δε μύθου τοῦδε κοινωνήσατε, and 167, δρω τομαΐον τόνδε βόστρυχον, the beginning of the 'secondary' delay. These words of Electra mean to the audience that the recognition is about to take place, and I venture to say that every Greek in the audience 'sits up and takes notice' accordingly. This 'secondary' delay continues through 211, where Electra says, πάρεστι δ' ώδις καὶ φρενῶν καταφθορά. By the locks of hair and the footprints Electra is almost convinced, and yet in doubt. For the resolution of this doubt Orestes appears at the psychological moment and the final act of recognition takes place, not only through Orestes' reiteration of the evidence already adduced, but by producing a piece of weaving (iδοῦ δ' υσασμα τοῦτο, 231), adding thereto all the expression of which a good actor 27 is capable. Thus ends the recognition, which occurs rather early in this play as compared with recognitions in Sophocles and Euripides. It suited Aeschylus' dramatic economy to make it thus. Surely there is no evidence that it fell flat. The reason for its early occurrence does not here concern me; and as it stands it supports my theory of a 'secondary' delay.

<sup>&</sup>lt;sup>25</sup> Throughout this inquiry I try to consider the matter from the point of view of the audience.

<sup>&</sup>lt;sup>26</sup> I quote the Oxford text, edited by A. Sidgwick.

<sup>&</sup>lt;sup>27</sup> I am inclined to believe that modern critics too often underestimate histrionic ability and effectiveness, which must have meant much to the Greeks.

# Sophocles.

# Electra.

The recognition scene in the Electra of Sophocles presents some striking differences as compared with that of the Choephori; first in the length of the 'primary' delay and in the skilful management of the 'secondary' delay made possible by the introduction of the urn filled with the supposed ashes of Orestes. The recognition is expected The audience knows that Orestes is present, and from the beginning. he heightens the interest by saying in 80, 28 ἀρ' ἐστὶν ἡ δύστηνος Ἡλέκτρα, upon hearing her ιω μοί μοι in 77, likewise by depositing locks of hair at his father's tomb (καρατόμοις χλιδαΐς, 52), which is particularly reinforced by the announcement of Chrysothemis in 900-901, ἐσχάτης δ' ὁρῶ Ι πυρᾶς νεώρη βόστρυχον τετμημένον, although developments have been such that Electra cannot on such evidence share the belief of her sister that Orestes has recently visited the tomb. Finally, the appearance of Orestes and Pylades (1098), face to face with Electra, must signify to the audience that the long delayed recognition is about to take place. At this point begins the 'secondary' delay, which is skilfully drawn out until Orestes is made to end it in 1221-1223, τηνδε προσβλέψασά μου σφραγίδα πατρὸς ἔκμαθ' εἰ σαφῆ λέγω.

# Oedipus Tyrannus.

<sup>28</sup> I quote the text of Dindorf.

<sup>29</sup> τούτου θανόντος νῦν ἐπιστέλλει σαφῶς | τοὺς αὐτοέντας χειρὶ τιμωρεῖν τινα.
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and we are brought to the 'secondary' delay at 1117 (ἔγνωκα γάρ, σάφ' ἴσθι Λαίου γὰρ ἢν | εἴπερ τις ἄλλος πιστὸς ὡς νομεὺς ἀνήρ) where the Theban herdsman is brought in and identified by the chorus. Then follows the triangular colloquy between the Corinthian, Oedipus, and the reluctant Theban herdsman, that brings us to the recognition (and  $\pi εριπέτεια$ ) in 1182 (ἰοὺ ἰού · τὰ πάντ' ἄν ἐξῆκοι σαφῆ, κτλ.), where Oedipus is finally convinced. Here again we find a well-defined case of a 'secondary' delay.

# EURIPIDES.

# Ion.

In this drama Euripides has tried his hand at complicating the plot, but has cheated the imagination of the audience by disclosing everything in the prologue. The 'primary' delay is purposely made long and handled with some skill, but I have no doubt that the audience marked the beginning of the 'secondary' delay, which really begins at  $1261^{30}$  ( $\tilde{\omega}$   $\tau avp \acute{o}\mu \rho \rho \phi v \ddot{o}\mu \mu a K_{\eta} \phi \mu \sigma o \tilde{v} \pi a\tau \rho \acute{o}s$ ,  $\kappa \tau \lambda$ .), where Ion, after the frustration and discovery of Creusa's plot to kill him, discovers her at the altar and prepares to kill her. This delay is further prolonged and accentuated by the necessity for the appearance of the Pythian priestess (1320,  $\tilde{\epsilon}\pi i\sigma \chi \epsilon s$ ,  $\tilde{\omega}$   $\pi a \tilde{\iota}$   $\kappa \tau \lambda$ .), whom the poet, in dire straits, has to call upon to produce the evidence  $\tilde{\sigma}$  whereby the recognition may be effected at 1437,  $\tilde{\omega}$   $\phi \iota \lambda \tau \acute{a}\tau \eta$   $\mu \omega \iota \mu \eta \tau \epsilon \rho$ ,  $\kappa \tau \lambda$ ., and 1439,  $\tilde{\omega}$   $\tau \acute{\epsilon}\kappa \nu \nu \nu$ ,  $\kappa \tau \lambda$ . Here we find another case of 'secondary' delay, and that rather long.

# Iphigenia in Tauris.

Likewise in this play Euripides, by his rather long prologue, acquaints the audience with the general situation. Immediately following Iphigenia's misinterpretation of her dream, whereby she concludes that her brother is dead, Orestes appears at 67 ( $\delta\rho a$ ,  $\phi i\lambda a\sigma \sigma \epsilon \mu \dot{\eta} \tau is \dot{\epsilon} \nu \sigma \tau i\beta \omega \beta \rho \sigma \tau \hat{\omega} \nu$ , words addressed to Pylades), and, in fact, is announced to the audience by Pylades in 71,  $\dot{\epsilon} \mu o i \gamma$ , ' $O \rho \dot{\epsilon} \sigma \tau a$ . Here begins the real 'primary' delay, which is well managed in view of the fact that Iphigenia and Orestes think each other dead. It is worthy of note in this connection to observe the epic flavor that Euripides gave the

<sup>30</sup> I quote the text of Nauek, 3d ed.

<sup>&</sup>lt;sup>31</sup> A recognition is effected in the Rudens of Plautus (1154 ff.) in a similar manner, apparently a direct imitation of the seene in the Ion; Creusa establishes her identity by describing, previous to seeing, the 'swaddling clothes' of her son; similarly, Palaestra describes certain *crepundia* in order to prove that she is the daughter of Daemones.

drama by giving the herdsman, who acts in the capacity of a herald, such a long speech (260-339) in which to report the capture of Orestes and Pylades; and thereby he adds to the delay before the recognition. No doubt the audience begins to suspect that the recognition is going to happen pretty soon after the herald's report of their capture; and certainly the searching questions, begun by Iphigenia at 472, τίς ὧρα μήτηρ ή τεκοῦσ' ὑμᾶς ποτε | πατήρ τ'; ἀδελφή 32 τ', κτλ., and continued at some length, reinforced by her decision (reached by her examination of the captives), to send a letter by one of the captives to her friends at Argos. etc., signify to the audience that the recognition scene is on. I should say, therefore, that the 'secondary' delay begins at 472, and that the recognition is really complete at 773, when Iphigenia says to Orestes, ηδ' ην όρᾶς σύ; but he is not allowed to declare himself until 795 (τω φιλτάτη μοι σύγγοι', κτλ.), when Iphigenia has finished reading the letter. Marking the real completion of the recognition at 773, we have before us a 'secondary' delay of three hundred verses in which the poet shows extraordinary skill in handling a delicate situation in a manner quite as satisfactory to the audience, I imagine, as to Aristotle, 33 who puts his stamp of approval upon this recognition scene. On this splendid scene, whereby Orestes recognized his sister, Euripides spent his force and had to resort to inferior means to make Orestes known to Iphigenia. From the very nature of the case (for the second recognition is but a necessary sequel to the first), there is no 'primary' delay to the second recognition, and therefore the short delay that does occur before the recognition, — a delay made necessary by the necessity of manufacturing convincing evidence, - must be called 'prefatory' rather than 'secondary.'

Helen.

The prologue to this play explains practically everything except the whereabouts of Menelaus. Perhaps the audience had a presentiment from the beginning that Menelaus would appear at the proper time, and that there would be a recognition. This latter is practically certain when Menelaus appears on the scene at 386, and particularly when he hears in 470 (Ἑλέινη κατ' οἴκους ἐστὶ, κτλ.) that Helen is in the house. At 528 Helen appears again, having learned from Theonoe that her husband is still alive, and everything is ready for the recognition. The 'secondary' delay begins at 541 (ἔα τίς οὖτος;), when Helen sights Menelaus, and leads up to the recognition that is completed at

 $<sup>^{32}</sup>$  Does not Euripides 'give the situation away' by not calling for an  $\dot{a}\delta\epsilon\lambda\phi\delta s$  ?  $^{33}$  Poetics, XVI, 11.

622–623, where Menelaus says, τοῦτ' ἔστ' ἐκεῖνο ' ξυμβεβᾶσιν οἱ λόγοι | οἱ τῆσδ' ἀληθεῖς, κτλ.

#### Electra.

I have purposely reserved for the last the consideration of the recognition scene of Euripides's Electra, which contains the disputed passage mentioned at the beginning of this paper. My consideration of this scene shows nothing very different from what has been noted in the other Euripidean recognition scenes. As usual, Euripides states his case in the prologue, and straightway brings on Orestes 34, who has paid a visit to his father's tomb during the night and made offerings of his hair, with the accompanying rites. The appearance of Orestes assures a recognition, and with the audience there is only the question of how Euripides will bring it about. They wondered, no doubt, how his treatment would differ from those of Aeschylus and Sophocles. Orestes meets Electra (220, μέν', ὧ τάλαινα, κτλ.) and assures her that her brother is alive but in exile (236), learns the status of the family affairs, assures himself of her willingness to assist in slaving the murderers of their father, learns that there is only one who would be able to identify him (287, πατρός γε παιδαγωγός άρχαῖος γέρων), after which he is about at a loss for words, when the peasant, the nominal husband of Electra, appears just in time to relieve the situation. After receiving an explanation about the presence of the strangers, he extends to them the hospitality of his home, for which he is censured by Electra, and despatched forthwith to the aged guardian 35 of Agamemnon to request that he lend material aid in providing a banquet for the stran-The peasant goes out at 430, and is not allowed to return. During the supposed meantime, which is a pretty short time, the chorus is called upon to entertain the audience until the old man  $(\pi\rho\epsilon\sigma\beta\dot{\nu}_s)$  can arrive with a young offspring of his flock 36, some fresh cheese and old wine. It happens, however, that the old gentleman has stopped by the tomb of Agamemnon, whereon he discovered the shorn locks of hair (515, ξανθής τε χαίτης βοστρύχους κεκαρμένους) which, he ventures to assert to Electra, may have been offered by Orestes, and thereby provokes a discussion with Electra that has given certain latter-day scholars considerable trouble.

With the situation thus before us, let us see about the 'secondary' delay before the recognition. As stated above, the audience is assured of a recognition by the presence of Orestes. It may be thought that

<sup>34</sup> S9 ff

<sup>35 409:</sup> ἔλθ' ως παλαιδν τροφόν ἐμοῦ φίλον πατρός.

<sup>36 494</sup> ff

the 'secondary' delay begins at 220, with the meeting of Orestes and Electra, but I am convinced that this whole scene between them, and even up to the arrival of the old man (487), is a part of the 'primary' I think the mention of the old man in the prologue is significant to the audience: that is, he is to play an important part in the drama, perhaps in the recognition scene; and this belief of mine is strengthened by the statement of Electra (285) that only one of her friends (the παιδαγωγός) would know Orestes — and, finally, the old man is to appear ostensibly for another purpose, but in reality to effect the recognition for which the parties concerned (Orestes and Electra) are present and ready when he arrives at 487 and inquires for Electra. I assume, therefore, that the eagerly awaited arrival of the old man is a signal, so to speak, to the audience that the recognition is about to be effected. Hence the 'secondary' delay begins at 487, and the recognition is actually completed in 577-578, when Electra says, συμβόλοισι γὰρ | τοις σοις πέπεισμαι θυμόν. It is not my purpose to discuss the disputed passage at length from an artistic point of view in order to combat the view of Mau, whom Mr. Tucker 37 follows; but I wish to call special attention to the fact that, even counting the disputed passage, the 'secondary' delay before the recognition is only 90 verses in length (from 487 to 577) — and even this can reasonably be shortened if we eliminate the introductory remarks of the old man about his provisions, etc., and make the weeping of the old man (501-502, έγω δε τρύχει τωβό έμων πέπλων κόρας | δακρύοισι τέγξας έξομόρ- $\xi_{\alpha\sigma}\theta_{\alpha\iota}$   $\theta_{\epsilon}\lambda_{\omega}$ ) the real signal for the beginning of the recognition scene, thus making the 'secondary' delay before the recognition 76 verses in length. In the first event we find a 'secondary' delay (i. e., from the time that the signal appears to be given to the audience that the recognition is about to take place until it is actually effected) of 90 verses; in the second event, a delay of 76 verses. By eliminating 518-544, the interpolated passage, according to Mau, my figures for the delay would become 63 and 49 respectively. Let us see how these figures compare with those given for 'secondary' delays found in other tragedies, especially those of Euripides.

'Secondary' delays before recognitions:

Aeschylus — Choephori: 235-165 = 70

Sophocles — Electra: 1221–1098 = 123

Oedipus Tyrannus : 1182-1117 = 65

<sup>37</sup> The Choephori of Aeschylus, Introd. p. lxxi ff.

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Euripides — Ion: 1437-1261 = 176

Iphigenia in Tauris: 773-472 = 301

Helen: 622-541 = 81

Electra: 577-487 = 90, or 577-501 = 76

By eliminating 518-544: 63
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From these statistics I am not disposed to draw any dogmatic conclusions. To my mind they only show in a general way (a) a tendency toward a lengthening of the 'secondary' delay (and, even this statement must be taken with some reservation, for I find it impossible, in view of the uncertain date of some of the plays, to reduce this matter to a chronological basis), particularly on the part of Euripides; 38 (b) 'secondary' delays of about equal length (accepting the full text of the Electra) in the Helen and the Electra, which appear to be plays of about the same date; (c) a 'secondary' delay in the Electra (rejecting the disputed passage) shorter than appears in any extant tragedy, and it seems to me unlikely that this should be the case. It appears that the very nature of the case is such in this 'secondary' delay of the Electra as to warrant the assumption that the audience would expect the loquacious old man to give a pretty full report 39 of his side trip to the tomb of Agamemnon, in spite of the fact that the poet apparently made use of it to criticise one of his predecessors.40

<sup>38</sup> This is especially true in the case of his better tragedies, to which distinction the Helen and the Electra can lay no claim.

<sup>&</sup>lt;sup>39</sup> Otherwise I fail to see any motive for mentioning his visit to the tomb.

<sup>&</sup>lt;sup>40</sup> In addition to the foregoing consideration of the bearing of delays before recognitions on our passage, I wish to add gratuitously at this point some observations made while pursuing my investigation, which may lend further weight to my final conclusion. In the first place, I believe that the locks of hair deposited on the tomb of Agamemnon, though primarily deposited as a religious act of filial duty, had become fixed in the Orestean legend as one of the recognized means of bringing about the recognition. Aeschylus skilfully followed the legend; Sophocles delicately acknowledged the legend with negative results in the case of Chrysothemis; Euripides acknowledged and expressed his disapproval of the legend. This assumption, if justified, makes it necessary to retain the disputed passage.

In the second place, why does Euripides use  $\sigma\nu\mu\beta\delta\lambda\omega\sigma$  (577) instead of  $\sigma\nu\mu\beta\delta\lambda\phi$ ? May it not be that Electra, perhaps unconsciously, includes the proofs or tokens in the disputed passage with the sear in 573? In other cases (cf. Or. 1130; Ion 1386) when Euripides uses  $\sigma\nu\mu\beta\omega\omega$ , the singular and plural seem to be properly differentiated.

Finally, in El. 568, after the  $\pi \rho \epsilon \sigma \beta \dot{\nu} s$  has said to her in the preceding verse,  $\beta \lambda \dot{\epsilon} \psi \nu \nu \nu \nu \dot{\epsilon} \dot{\epsilon} s$   $\tau \dot{\epsilon} \nu \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ ,  $\dot{\epsilon} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu} \dot{\nu}$ . Now, what is the force of  $\pi \dot{\alpha} \lambda a \iota$  here (cf. its use in El. 357, where the reference is certain), and, in fact, the justification of the statement, if

In summarizing the results of my investigation it appears (1) that there is sufficient evidence, in both epic and tragic poetry, for 'primary' and 'secondary' delays before ἀναγνωρίσεις; (2) tendency to lengthen the 'secondary' delay, presumably for dramatic effect —a tendency that is strikingly illustrated by Euripides in contrast with Aeschylus and Sophocles; (3) there is no reason to expect an abnormally short 'secondary' delay in the Electra of Euripides, but rather the contrary. in order to give the old man an opportunity to satisfy the natural curiosity of Electra and the audience by giving them a detailed account of his startling discoveries at the tomb of Agamemnon an opportunity that is met, in part, by the passage in question. conclusion, therefore, I have no hesitancy in accepting the disputed passage (El. 518-544), considering it so much bombast (to delay the recognition), wrongly employed by an indiscreet poet for critical purposes — a passage that 'smacks' 41 not 'of the age of Zoilus,' but of the age and flavor of Socrates and Aristophanes, the latter of whom might well have preferred charges against Euripides for encroaching on his literary province.

there is not a reference to the old man's statements in the disputed passage? It appears to me that the whole verse is a kind of reiteration and echo of Electra's reproach in 524, oùx &&i årdρόs, & γέρον συφοῦ λέγεις.

<sup>41</sup> Tucker's Choephori, p. lxxii.



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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A NEW METHOD FOR THE DETERMINATION OF THE SPECIFIC HEATS OF LIQUIDS.

BY THEODORE WILLIAM RICHARDS AND ALLAN WINTER ROWE.

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# A NEW METHOD FOR THE DETERMINATION OF THE SPECIFIC HEATS OF LIQUIDS.

BY T. W. RICHARDS AND A. W. ROWE.

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During the course of an extended research upon heats of neutralization now in progress, it became necessary to devise some method for the accurate determination of the specific heats of the reacting solu-Obviously an accurate value for any thermochemical measurement can only be obtained when the factors involved in the calculation are accurately ascertained; and it is well known that the existing data on this subject are by no means satisfactory. The recognized sources of error of the majority of the earlier methods and the discrepancies observed in the values obtained by the different experimenters using them 1 limit any dependence which can be placed in the constants thus obtained. Further, the truth of the assumptions upon which the corrections for their errors are based is by no means adequately proved. To obviate the necessity of these corrections, and thus eliminate the uncertainty attending their use, a new method has been devised. A brief discussion of the earlier forms of apparatus may assist in a better understanding of the difficulties encountered in devising this method and the means by which they were surmounted.

Of the various methods recorded, that of Andrews<sup>2</sup> has been, perhaps, the most frequently used. This depended upon the transference of a heated object or "calorifer" from a source of heat to the calorimeter, which contained either water or the liquid to be studied. A compar-

### Specific Heat of NaOII

| %    | Sp. Ht. | Observer. |
|------|---------|-----------|
| 49.5 | 0.816   | Hammerl,  |
| 25.6 | 0.869   | Hammerl.  |
| 22.9 | 0.847   | Thomsen.  |

<sup>&</sup>lt;sup>2</sup> Pogg. Ann., **75**, 335 (1848).

<sup>&</sup>lt;sup>1</sup> The following is a typical example:

ison of the observed rise with water and with the liquid under investigation gave a simple means of determining the relative heat capacities. A variant of this method consisted in using either water or the studied liquid in the calorifer, the calorimeter always being filled with the former. This method, with various independent modifications, was used by Schüller,<sup>3</sup> Person,<sup>4</sup> Pfaundler,<sup>5</sup> Marignac,<sup>6</sup> Hammerl,<sup>7</sup> and a number of other investigators. The simplicity of this procedure, and the elimination of many doubtful factors by using comparative results, are strong arguments for its use; but the interchange of heat by radiation between both the calorifer and the calorimeter and their environments, coupled with the unavoidable lag of the thermometer, introduces elements of uncertainty fatal to the highest accuracy.

The ingenious device of Thomsen, whereby measured amounts of hydrogen are burned, under constant pressure, inside the calorimetric system, gave concordant results; but the values obtained are subject to some of the same corrections as those demanded by the Andrews method. Pfaundler, using electrical energy as his source of heat, attempted automatically to eliminate the radiation-correction by heating simultaneously two calorimeters, one containing water, the other the liquid under investigation. If the rise of temperature were the same, the loss by radiation would cancel. But as varying heat capacities involve varying amounts of electrical energy to secure this result, the electrical heat unit enters the computation, and by its uncertainty detracts from the absolute accuracy of the determination. This device has been recently applied in a modified form by Magie <sup>10</sup> with considerable success; but it is by no means easy to find a heat-producing electrical resistance suitable for immersion in electrolytes.

Several other different methods have been suggested by others, but these also are not wholly free from defect. In one, the radiation method of Dulong and Petit, <sup>11</sup> the hot object was enclosed in an evacuated and blackened chamber, losing its heat by radiation. The chamber was placed either in an ice bath or in a water bath of sufficient size to be unaffected by the heat given up by the cooling object. The relative temperatures of the hot object and its environment, and

<sup>&</sup>lt;sup>3</sup> Ann. de Chim. et Ph., **3**, 33, 437.

<sup>4</sup> Pogg. Ann., **136**, 70, 235 (1869).

<sup>&</sup>lt;sup>6</sup> Wien. Ber., **62**, (2), 379 (1870).

<sup>&</sup>lt;sup>6</sup> Arch. Gen., 2, 39, 217 (1870); 2, 55, 113 (1876).

<sup>&</sup>lt;sup>7</sup> C. R., **90**, 694 (1880).

<sup>&</sup>lt;sup>6</sup> Thermochem. Untersuch., 1, 24 et seq. (1882); Pogg. Ann., 142, 337 (1871).

<sup>&</sup>lt;sup>9</sup> Wien. Ber., **59**, (2), 145 (1869); **100**, (2a), 352 (1891).

<sup>&</sup>lt;sup>10</sup> Phys. Rev., **9**, 65 (1899); **13**, 91 (1901); **14**, 193 (1902); **17**, 105 (1903).

<sup>&</sup>lt;sup>11</sup> Ann. de Chim. et Ph., 2, 10, 395 (1819).

the time required to secure thermal equilibrium, gave the necessary data. The uncertainty of the true law of cooling is enough to seriously impair the accuracy of any results thus obtained, however.

Quite a different procedure was adopted by Hesehus, <sup>12</sup> who balanced the heating effect of the calorifer in a calorimeter at room temperature by the additions of successive portions of cold water. In this way he eliminated any cooling of the calorimeter. Waterman <sup>13</sup> improved this method, and made a series of apparently excellent determinations of the specific heats of metals. Using a Pfaundler resistance coil as a source of heat, Litch <sup>14</sup> has studied in this way the specific heat of water. Satisfactory as these methods may appear upon first sight to be, however, the unavoidable warming of the cold water during its transference to the warm calorimeter introduces an element of uncertainty just as great as the uncertainty in the ordinary cooling correction; hence no real gain was made. The method is not really adiabatic.

In 1905 a new method was described by Richards and Lamb, <sup>15</sup> eliminating most of the earlier sources of error while maintaining all the advantages of the older procedure except simplicity. Two portions of liquid — one hot, the other cold — were rapidly discharged from their respective containers and mixed in a calorimeter, the temperature of the mixture being that of the environment. Obviously, the cooling experienced by the warm liquid during transference is balanced by the warming of the cold liquid. The method involves a somewhat high degree of mechanical complexity, and is further complicated by the necessity of making supplementary determinations of the heats of solution or dilution where the two liquids possess any degree of mutual solubility.

More recently a new method of calorimetry, by a strictly adiabatic procedure, has been described by Richards, <sup>16</sup> and its applicability has been experimentally proved by the same investigator with the assistance of Forbes, <sup>17</sup> Henderson, <sup>18</sup> and Frevert. <sup>19</sup> Here the *environment* of the calorimeter is caused to increase in temperature as the calorimeter itself becomes warmer. The studied transformation in the calorimeter thus takes place without interchange of heat with the surroundings. Further, since both the initial and the final temperatures are stationary, the error due to the lag of the thermometer disappears.

<sup>12</sup> Jour. Soc. Ph. Chim. Russ., Nov., 1887; Jour. de Phys, 7, 489 (1888).

<sup>13</sup> Phys. Rev., 4, 161 (1896).
17 Ibid., 41, 10 (1905).

<sup>&</sup>lt;sup>14</sup> Ibid., **5**, 182 (1897). 
<sup>18</sup> Ibid., **41**, 10 (1905); **42**, 573 (1907).

<sup>&</sup>lt;sup>15</sup> These Proceedings, **40**, 659 (1905). <sup>19</sup> Ibid., **42**, 573 (1907).

<sup>16</sup> Ibid., 41, 8 (1905).

The use of this method obviates at once the greatest source of error in calorimetric work of all kinds, namely, the correction for cooling. As the method may be employed in any kind of calorimetric work, there seemed to be no reason why it should not be applicable to work on specific heats; and the present paper will show that it is indeed of great service there. The application is extremely simple: the substance to be studied should obviously be placed in a calorimeter surrounded on all sides by a jacket, the temperature of which can be changed to correspond exactly with the warming of the substance by some known source of heat.

It was first necessary to decide upon the exactly quantitative source of energy to be used for heating the substance within the calorimeter. Some experimenters have used merely the heat of a warmer body; others have used electrical heat; and Thomsen availed himself of the heat of combustion of hydrogen. Of course many other chemical reactions might be employed for this purpose, as Ostwald and Luther have pointed out <sup>20</sup>; and after much consideration there was selected for this present work the heat of neutralization of pure sulphuric acid and sodic hydroxide as the most convenient, especially because it is not very changeable with the temperature.

Definite amounts of acid and alkali were allowed to react in a platinum flask surrounded by the liquid in the calorimeter, and the rise of temperature in the whole system was carefully noted. By comparing the rise of temperature under these conditions with the rise shown when pure water is in the calorimeter, a comparative measurement of the heat capacity of the liquid is made. A few words will suffice to explain the disposition of the apparatus and the method of its use.

#### Apparatus.

A diagrammatic sketch of the apparatus in vertical section is seen in Figure 1. First, the environment of the calorimeter will be described. The jacket (A) was made of heavy sheet copper and was provided with an outflow cock (V) for convenience in emptying. The soldered joints were heavily coated with shellac to prevent corrosion by the alkaline solution with which it was filled. The capacity was 17.5 liters. A rotary, vaned stirrer (R), with a speed of 145 turns per minute, insured thermal homogeneity in the contents of the jacket. To raise the temperature, crude sulphuric acid was run into the jacket through the funnel (F), into the alkali contained in the jacket, and the heat of neutralization thus liberated was rapidly disseminated throughout

<sup>20</sup> Ostwald-Luther, Phys. chem. Messungen (1902), p. 204.

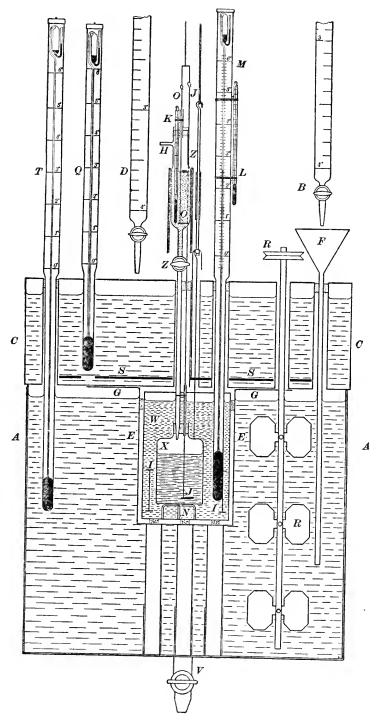


FIGURE 1.

the entire mass of liquid. The acid was contained in the burette (B) empirically graduated to give a rise of 0.1° for each scale division. The Beckmann thermometer (T), graduated in twentieths of a degree. indicated the temperature. The cover (C) was similarly constructed. the capacity being 6 liters. It was furnished with an oscillating stirrer (S) with a speed of 45 strokes per minute, and the Beckmann thermometer (Q) similar to that in the jacket. In the same way acid was admitted from the burette (D), suitably graduated. Copper tubes, permitting the passage of those portions of the apparatus which projected below the cover, were soldered to the bottom, and the joints were protected by a coating of shellac. The cover must fit tightly, otherwise evaporation will cause a slight cooling effect. The vessel was thoroughly cleaned at the end of each day's work. The inner cylinder (E) used to hold the calorimeter proper, was of sheet copper, nickel plated, and burnished on the inner surface. It was mounted on three legs, fitting into holders soldered to the bottom of the jacket, and was provided with the ring or apron (G), which prevented any portion of the liquid in the jacket from being thrown by the rapid stirring into its interior space.

Inside this inner cylinder and separated from it by points of dry cork was the calorimeter proper (W). This was a platinum can of 0.7 liter capacity, weighing 107 grams. During an experiment this was filled with water, or with the liquid the specific heat of which was to be measured. Thermal homogeneity of the calorimeter contents was secured by the two-stage perforated platinum stirrer (I) driven at a speed of 45 oscillations per minute. The temperature was accurately indicated by a large-bulbed, Beckmann thermometer (M), which was graduated in hundredths of a degree and capable of being read within  $\frac{1}{1000}$ . A small auxilliary thermometer (L) gave the temperature of the exposed stem. Thus far the apparatus is essentially similar to that used by Richards, Henderson, and Frevert.

The heat-producing system presents the chief novelty. It was made up of two parts, a bottle (X) and a burette (Z). The former was made of platinum, with a capacity of 0.17 liter and weighing 52.64° grams. In this was placed a definite weight of a somewhat dilute, exactly known solution of sulphuric acid. The liquid was agitated by the platinum stirrer (J), alternating 145 times per minute. The bottle rested upon the glass triangle (N), thus permitting a free circulation of the calorimeter liquid around the entire surface. Tightly fastened into the neck by a small rubber stopper was the tip of the burette (Z), which contained a concentrated solution of soda. The discharge of this solution into the acid, and the consequent heat evolved

by the reaction, formed the heat-producing action upon which the method is based. Since the alkali was the only part of the reacting system which, from its position, night, at the beginning of an experiment, have a different temperature than that of the remainder of the system, one needed to measure its temperature accurately. To this end the thermometer  $(K)^{21}$  was immersed in the liquid, in which the stirrer (O) oscillated 145 times per minute. Concentric layers of heavy white silk aided in protecting the liquid mass from outside fluctuations of temperature. The drainings which collected in the lower end of the delivery tube after the admission of the soda to the bottle were expelled by blowing with a rubber bulb through the side tube (H).

It is of the utmost importance that the stirring should be efficient. The entire system of stirrers was driven by a small electric motor, a

system of wooden pulleys giving the required reductions in speed. The stirrers of the bottle, jacket, and burette formed one system, and those of the calorimeter and cover, a second. It was found advantageous to attach the various oscillating stirrers to metal rods working in sleeves and actuated by cords fastened eccentrically to the proper pulleys. In this way uniformity of travel and stroke were secured, the friction of the rods in the sleeves being reduced by good lubrication to a negligible quantity.

As uniformity of composition in the acid used in the bottle within the inner vessel of the calorimeter is a fundamental condition for the accuracy of the process, the familiar device shown diagrammatically in Figure 2 was used for delivering it. The acid was stored in the 2-litre Jena flask (A) closed with a perforated rubber stopper. Through the siphon (S) the acid could be drawn into the burette (B). The

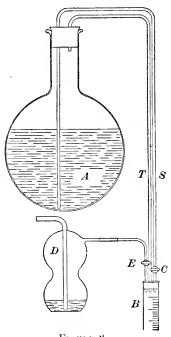


FIGURE 2.

auxiliary tube (T) equalized the pressure in the two containers. After

<sup>21</sup> The thermometer was a very accurate one, made especially for this purpose. It has a range of but 8 degrees, graduated in tenths.

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filling the burette, the inflow  $\operatorname{cock}(C)$  was closed. When the acid was to be drawn from the burette, the  $\operatorname{cock}(E)$  connecting with the outside air through the wash bottle (D) was opened and the pressure thus equalized. As the wash bottle was filled with acid of the same concentration as that in the reservoir, the tension of aqueous vapor of the air introduced was the same as that obtaining in the system. The flask was always shaken before anything was drawn from it. By this means an acid was secured of unvarying composition, as shown by numerous experiments. In a similar way, with the addition of a sodalime tower for the removal of carbon dioxide, the alkaline solution was maintained at constant strength.

It is needless to say that the thermometers were compared with Sevres standards with the greatest care, especially that designated M. Successive standardizations at different times were gratifyingly concordant.

### CONDUCT OF AN EXPERIMENT.

The calorimeter proper (W, Figure 1) was partly filled with about 0.47 litre of the desired liquid, - either pure water to serve as a standard, or a solution to be studied. It was then brought to the temperature selected for the experiment, accurately weighed, and placed inside the jacket (E. Figure 1). This latter contained its charge of dilute crude alkaline solution, and was also near the selected initial temperature. About 0.1 litre of pure acid (1.34 normal) was then run into the platinum bottle (A, Figure 1), weighed carefully, and placed in a thermostat to bring it to the desired temperature. The innermost short burette (Z) was filled to the mark with about 0.02 litre of pure alkaline solution and brought near the required temperature. The whole apparatus was then rapidly assembled in the form already described. minutes after the stirrers were put in operation, the whole system was in thermal equilibrium, as was shown by the constant readings of the various thermometers. The temperatures of the calorimeter and the pure alkaline solution, indicated by the thermometers M and K respectively, were then carefully recorded, the stirrer in the bottle was disconnected, and the pure alkali discharged into the bottle as rapidly as possible. The immediate temperature rise, as the heavy alkali sank through the acid, was paralleled outside by running acid into jacket and cover. The bottle-stirrer (J) was then agitated by hand, this permitting excellent control of the mixing of pure acid and alkali and the resulting rise in temperature. When the mixing was almost complete, as shown by the rise of the thermometer M, the stirrer was reconnected with the motor and the final mixing done mechanically. The changes in the calorimeter throughout the experiment were carefully duplicated in the jacket and cover. At the end of some nine minutes the final equilibrium was attained, the thermometer readings becoming constant, at a temperature about four degrees above the initial temperature.

The calculation was exceedingly simple except for two features, each of which concerned the sodic hydroxide. The first of these was a correction needed because the alkaline solution had not exactly the temperature of the calorimeter at the moment of delivery. If warmer. the alkali brought with it a slight excess of heat; if cooler, it caused a slight deficiency. This correction was easily calculated by multiplying the water equivalent of the alkaline solution by the difference of temperature. When the alkali was too warm, this small product was subtracted from the total; when too cold, added. The other unusual feature involved not the total amount of alkali, but only the excess of this solution over and above the constant amount (19.30 grams) needed to neutralize the acid. It was intended that the alkaline solution should be of such concentration as to evolve enough heat on dilution to raise itself through the range of temperature of the experiment. If this were the case, it would not be necessary to know very exactly the amount of the alkali; any excess would not affect the final temperature. The alkali was made up as nearly as was possible on the basis of the previously known data to accomplish this result, and was nearly enough so for the present purpose. Its concentration was 8.97 normal.

The data and calculation of a specimen experiment may now be given without further preamble.

# SPECIMEN EXPERIMENT WITH WATER IN CALORIMETER.

No. 4, February 27, 1908.

## Data concerning temperature:

| Initial temperature of calorimeter              | 16.489° |
|-------------------------------------------------|---------|
| Final temperature of calorimeter                | 20.237° |
| Rise of temperature during experiment           | 3.748°  |
| Temperature of sodic hydroxide                  | 16.44°  |
| Difference between this and initial temperature | 0.05°   |

# Data concerning heat capacity, expressed in terms of the water-equivalent: Water in calorimeter 474.97 graph

| Water in calorimeter                            | TITO SIM.   |
|-------------------------------------------------|-------------|
| Calorimeter and fittings, equivalent to .       | 11.35 "     |
| 103.71 grm. of dilute acid (sp. ht. $= 0.94$ ). | 97.49 "     |
| 19.3 grm. alkaline solution needed to neu-      |             |
| tralize acid (sp. ht. = $0.84$ )                | 16.21 "     |
| Total heat capacity                             | 600.02 grm. |

| Total heat observed = $600.02 \times 3.748^{\circ}$               | 2248.87 cal. (18°) |
|-------------------------------------------------------------------|--------------------|
| Correction for heat needed to warm 20.9                           |                    |
| grm. alkaline solution through $0.05^{\circ}$                     | +0.88 "            |
| Total heat, corrected, from neutralization of 103.71              |                    |
| grams acid                                                        |                    |
| Heat evolved from 100 grm. dilute acid = $\frac{2249.75}{1,0371}$ | 2169.3 cal.        |

This process was repeated until there seemed to be no doubt as to the exact amount of heat evolved by the heat of neutralization of exactly 100 grams of this particular dilute acid by a slight excess of this particular alkaline solution under these perfectly definite conditions. The data and results of a series follow.

In the following table,  $T_1$  is the initial temperature of the system and  $T_2 - T_1$  is the observed rise. The other values are self-explanatory.

| No.        | $\mathrm{H}_2\mathrm{SO}_4$ | Total Water<br>Value. | NaOH<br>Correction. | T <sub>1</sub> .      | $T_2 - T_1$ . | Corrected<br>Heat.                    | Heat per<br>100 grams.   |
|------------|-----------------------------|-----------------------|---------------------|-----------------------|---------------|---------------------------------------|--------------------------|
| <b>4</b> a | grams.<br>103.74            | grams.<br>597.19      | calories4.74        | Centigrade.<br>16.03° | Centigrade.   | calories (18°) <sup>*</sup><br>2250.3 | calories (18°)<br>2169.1 |
| 5a         | 103.74                      | 597.19                | -3.51               | 16.37°                | 3.7740        | 2250.3                                | 2169,1                   |
| 2          | 103.69                      | 600.02                | +7.02               | 16.26°                | 3.736°        | 2248.7                                | 2168.7                   |
| 3          | 103.68                      | 599.98                | +5.44               | 16.37°                | 3 7400        | 2249.4                                | 2169.5                   |
| 4          | 103.71                      | 600.02                | +0.88               | 16.49°                | 3.7480        | 2249.8                                | 2169.3                   |
|            |                             | <u>I</u>              | Me                  | an                    |               |                                       | . 2169.14                |

RESULTS WITH WATER.

The maximum variation from the mean here is only 8 parts in 22,000, or about 0.02 per cent. As will be seen upon inspection, the correction for the difference in temperature of the alkali is sometimes additive and sometimes subtractive in the different experiments, hence the concordance of the observed results in connection with these values is excellent testimony as to the accuracy of the correction.

The amount of heat evolved by the neutralization of 100 grams of sulphuric acid under these conditions was now used as the standard in warming various definite solutions through about the same range of temperature. In order to accomplish this purpose, the solutions

102.79 cm

were successively placed in the calorimeter, and the flask for conducting the heat-producing neutralization was immersed in each just as it had previously been immersed in the pure water.

As an example, a series of results with a special solution of hydrochloric acid may be given. This acid was chosen for determination because, being involved in another research, its specific heat was a matter of immediate interest.

Below are given the data and method of calculating a single experiment, as well as the data of a series.

### SPECIMEN EXPERIMENT WITH A SOLUTION.

No. 3, May, 1908.

III : alt of Allute malaburia and in alutinum buttle

| Weight of dilute sulphuric acid in platinum bottle . 103.42 grm.                   |
|------------------------------------------------------------------------------------|
| Data concerning temperature:                                                       |
| Initial temperature 16.236°                                                        |
| Final temperature 19.960°                                                          |
| Temperature rise $3.724^{\circ}$                                                   |
| Temperature of alkali 16.13°                                                       |
| Excess over initial temperature —0.11°                                             |
| Heat, producing this effect:                                                       |
| Calculated heat evolved by reaction =                                              |
| $103.72 \times 2169.14 \dots \dots 2249.83 \text{ cal. } (18^{\circ})$             |
| Heat taken by alkali = $20.9 \times 0.84 \times 0.11$ -1.93 "                      |
| Total heat actually available in process 2247.90 cal.                              |
| Data concerning heat capacity, in terms of water equivalent: 22                    |
| Water value of calorimeter 10.87 grm.                                              |
| Water value of acid 97.50 "                                                        |
| Water value of alkali 16.21 "                                                      |
| Total                                                                              |
| Heat used by system exclusive of solution = $124.58 \times$                        |
| $3.724^{\circ}$ = 463.94 cal. (18°)                                                |
| Heat needed to raise 488.35 grams of hydrochloric<br>acid contained in calorimeter |
| $=2247.90 - 463.94 = 1783.96 (18^{\circ})$                                         |
|                                                                                    |

<sup>22</sup> As these amounts are constant in all the determinations, slight constant errors in them would have only a vanishingly small pernicious effect upon the final results. The method is a comparative one, and small errors of this kind cancel out.

Hence, specific heat of hydrochloric acid of concentration HCl 200.0 
$$H_2O = \frac{1784.0}{488.35 \times 3.724} = 0.9809$$

The experimental data for this series are found in the accompanying table. Several experiments where the manipulation was faulty were rejected, but if they had been included the average would have remained essentially unchanged.

| No. | нсі.             | H <sub>2</sub> SO <sub>4</sub> . | T <sub>NaOH</sub> . | Т1.    | $T_2 - T_1$ . | Correction<br>NaOH. | Specific<br>Heat. |
|-----|------------------|----------------------------------|---------------------|--------|---------------|---------------------|-------------------|
| 5   | grams.<br>488.31 | grams.<br>103.71                 | 16.38°              | 16.39° | 3.7270        | calories.           | 0.9810            |
| 6   | 488.25           | 103.68                           | 16.14               | 15.99  | 3.732         | +2.63               | 0.9806            |
| - 8 | 488.35           | 103.72                           | 16.13               | 16.24  | 3.724         | -1.93               | 0.9809            |
| 9   | 488.34           | 103.70                           | 16.30               | 16.40  | 3.723         | -1.76               | 0.9812            |
|     |                  | 1                                | M                   | ean    |               |                     | 0.9809 23         |

The Specific Heat of HCl 200  $\mathrm{H}_2\mathrm{O}$ .

As will be seen, the maximum variation from the mean is 0.03 per cent. This experimental error is as low as could possibly be expected.

### HEAT OF DILUTION.

It is obvious that this apparatus can be applied to the accurate determination of the heat of dilution of any solution put into the burette (Z), if water instead of sulphuric acid is placed in the platinum flask (X). The liquid to be diluted is run into the bottle as before, and there mixes with a weighed amount of pure water. A series of three experiments on the dilution of a concentrated solution of sodic hydroxide is given below. The results are calculated in kilojoules, as the best standard for permanent record; in the experiments previously recorded this was unnecessary because the method was a comparative one and the dimension of heat energy was eliminated in the result. 0.100 litre of pure water was contained in the platinum bottle.

<sup>&</sup>lt;sup>23</sup> The corresponding values obtained from the results of Thomsen (loc. cit.) and Marignac (loc. cit.) are respectively 0.979 and 0.983.

| No. | Water Value. | NaOH.  | $T_2-T_1$ . | Corr. (NaOH). | Heat evolved by Dilution to NaOH $\cdot$ 43.5 H <sub>2</sub> O. |
|-----|--------------|--------|-------------|---------------|-----------------------------------------------------------------|
|     | grams.       | grams. | ° C.        | calories.     | kilojoules.                                                     |
| I   | 601.79       | 21.39  | 0.132       | - 4.5         | 3.82                                                            |
| 2   | 601.86       | 21.43  | 0.129       | - 3.2         | 3.78                                                            |
| 3   | 602.01       | 21.59  | 0.155       | -18.5         | 3.77                                                            |

THE HEAT OF DILUTION OF SODIC HYDROXIDE NaOH: 5.85 H2O.

The variation from the mean falls within the probable experimental error (0.001°).

Obviously any thermochemical effect produced by the mixing of two liquids could be measured in the same way. It is to be noted that the method has a great advantage over other methods in that great speed in the execution of the experiment is not at all necessary. By the old methods, speed was essential because of the correction for cooling; but here there is no correction for cooling because the performance is strictly adiabatic. The reaction may extend over hours, if necessary.

It should be noted that the correction concerning the sodic hydroxide could be wholly avoided if the pure alkaline liquid were contained in a receptacle within the calorimeter, instead of being held in a burette above it. Such a receptacle has been used successfully by Richards and Henderson <sup>24</sup> and was not introduced in these preliminary experiments on account of its slightly greater complexity. In the future it will be adopted, and with it we hope to secure yet more accurate results.

Experiments are now under way for the determination of the specific heats and heats of dilution of various solutions at different concentrations and at different temperatures, by the methods just described.

It is a pleasure to acknowledge the generous aid of the Carnegie Institution of Washington, without which we should have been greatly hampered in this work. The present and future results of this investigation will be published in greater detail by that Institution, in one of its shortly forthcoming regular publications.

<sup>&</sup>lt;sup>24</sup> These Proceedings **41**, 11 (1905); Zeit. phys. Chem., **52**, 551 (1905).

### SUMMARY.

The results of this paper may be briefly summarized as follows:

- 1. A new method for the accurate determination of the specific heats of liquids has been described, using the adiabatic calorimeter and a chemical source of heat.
- 2. The heat capacity of a solution of hydrochloric acid of molal concentration  $HCl + 200 H_2O$  has been measured.
- 3. The method has been applied to the accurate determination of heats of dilution.
- 4. A solution of alkali was used whose heat of dilution automatically compensates for any excess which might have been added.

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PISISTRATUS AND HIS EDITION OF HOMER.

BY SAMUEL HART NEWHALL.



### PISISTRATUS AND HIS EDITION OF HOMER.

#### BY SAMUEL HART NEWHALL.

Presented by M. H. Morgan. Received May 13, 1908.

In dealing with the life and works of any great character in history, especially a man whose figure in the world has conceivably been magnified through the mists of distant time, it is essential carefully to discriminate between fact and fable, between a clear statement, however incidental, found in any reliable writer, whether he makes the assertion on his own authority or on that of some author known to us, and a mere tradition to which the writer refers without stating his authority, however prevalent the story may have been in his own lifetime, and even for many years previous. For it is possible, though not perhaps probable, that a tradition could be very old and very widespread without having the slightest foundation on fact. In dealing, then, with the literary work of Pisistratus, a prominent and influential person in the early days of Hellas, it is especially necessary to distinguish between uncompromising statements made by authorities concerning his work, and mere references to a commonly accepted tradition introduced by such listless preludes as οί παλαιοί φασιν and similar expressions. In this article I shall try to make a satisfactory answer to two questions: first, did Pisistratus really do any literary work in connection with the Homeric poems? and, secondly, how thorough and, so to speak, professional were his services? that is, did he produce a text edition of the Iliad and the Odyssey? These questions are by no means new, but it is time that they were once more considered together, and perhaps something new may be brought forward in answering them.

First, I desire to present a few passages from the ancient authors which point to a certain amount of literary activity on the part of Pisistratus in connection with the Homeric poems, though they could not be considered indicative of anything so thorough and systematic as a regular edition. Strabo, the geographer, who manifests a wide interest in literature, briefly tells the following story (IX, 394, 10): καί φασιν οἱ μὲν Πεισίστρατον, οἱ δὲ Σόλωνα παρεγγράψαντα ἐν τῷ νεῶν καταλόγω μετὰ τὸ ἔπος τοῦτο, Αἴας δ' ἐκ Σιλαμῶνος ἄγεν δυοκαίδεκα νῆας, έξῆς τοῦτο,

στησε δ' ἄγων, ῖν' ᾿Αθηναίων ἵσταντο φάλαγγες, μάρτυρι χρήσασθαι τῷ ποιητῆ τοῦ τὴν νῆσον ἐξ ἀρχῆς ᾿Αθηναίων ὑπάρξαι. This bit of evidence, if true, though we must bear in mind that it is based on tradition, and that, too, tradition which ascribes an act to either one of two men, points to an insertion which might more properly be called malicious than literary. This inserted line, popularly said to have been an interpolation, is verse 558 of the Iliad B, and stands in all known manuscripts, with the exception of seventeen. But in the best manuscript it is lacking, as La Roche points out in his edition of the Iliad.<sup>2</sup> By "the best manuscript" I understand him to mean the Venetus A. Accordingly, in his text, he encloses this line in brackets. Aristotle also, in his Rhetoric, makes Homer, as a writer of historical accuracy, the final court of appeal for the Athenians in their contest for the possession of the much-disputed Salamis, though unfortunately he does not mention the name of Pisistratus: περὶ δὲ μαρτύρων, μάρτυρές εἰσι διττοί, οἱ μὲν παλαιοί, οι δε πρόσφατοι, και τούτων οι μεν μετέχοντες του κινδύνου, οι δ' εκτός. λέγω δὲ παλαιοὺς μὲν τούς τε ποιητὰς καὶ ὅσων ἄλλων γνωρίμων εἰσὶ κρίσεις φανεραί, οξον 'Αθηναίοι 'Ομήρω μάρτυρι έχρήσαντο περί Σαλαμίνος. mark of Aristotle's, of course, has no direct connection with Pisistratus. I quote it here merely to show that at least Strabo's story of the use of Homer as a witness in the dispute about Salamis is true on the authority of Aristotle. In Quintilian (V, 11, 40) we have a slightly more pertinent reference to the same circumstance. His words are these: neque est ignobile exemplum (i. e. of auctoritas) Megarios ab Atheniensibus, cum de Salamine contenderent, victos esse Homeri versu, qui tamen ipse non in omni editione reperitur, significans Aiacem naves suas Atheniensibus iunxisse. Here we see the verse in question is quoted in a translation with the added suggestion that perhaps it is not genuine from the fact that it is not contained in all the manuscripts. This statement, however, about the use of Homer as historical testimony may very well have been made by Quintilian on the authority of Strabo, his predecessor, Quintilian's own more intimate and critical literary knowledge prompting him to note the omissions in certain manuscripts, with which Strabo, very naturally, was unfamiliar.

On the authority of Hereas, a Megarian writer of uncertain date, we are informed by Plutarch (Theseus, XX) that Pisistratus inserted verse 630 of the eleventh book of the Odyssey: Δεινὸς γάρ μιν ἔτειρεν ἔρως Πανοπηΐδος Αἴγλης. Τοῦτο γὰρ τὸ ἔπος ἐκ τῶν Ἡσιόδου Πεισίστρατον ἐξελεῖν Φησιν

<sup>&</sup>lt;sup>1</sup> Cf. T. W. Allen in Class Rev., XV, p. 8 (1901).

<sup>&</sup>lt;sup>2</sup> Footnote to Il., II, 558.

<sup>3 1,</sup> p. 1375, 26.

Ήρεας ὁ Μεγαρεύς, ωσπερ αὖ πάλιν ἐμβαλεῖν εἰς τὴν Ὁμήρου νεκυίαν τό, Θησέα Πειρίθοον τε θεων αριδείκετα τέκνα, χαριζόμενον 'Αθηναίοις. The manuscripts, according to La Roche. 4 read in this place, ἐρικυδέα for ἀριδείκετα, which change he himself adopts in his edition, explaining the variation by the well warranted supposition that either Hereas or Plutarch, in accordance with the prevailing custom of the ancients, was quoting from This passage shows that even before the time of Plutarch it was believed by one writer at least that Pisistratus inserted this verse in the Odyssey. Düntzer,<sup>5</sup> then, has some warrant for his supposition that in the time of Hereas credence was given to the story of the Pisistratean edition of the Homeric poems, provided we take it for granted that the poems did not exist in writing before the time of Pisistratus, — a point on which authorities differ. If they had previously been reduced to manuscript form, then the insertion of a line by a ruler, merely to tickle the vanity of his subjects, can hardly be considered indicative of an entire recension of the poems.

Ascribed to Dieuchidas, the Megarian historian, we find a statement which, though vague, has reference, nevertheless, to an activity of some sort on the part of Pisistratus in connection with the Homeric poems. The exact date of Dieuchidas himself is a matter of some uncertainty, though he is confidently placed by Wilamowitz 6 in the fourth century B. C., and by W. Christ, who refers to Wilamowitz, among the earlier Atticists, which would make his sphere of activity fall in the first part of the third century B. C. The statement is contained in Diogenes Laertius (1, 57), and reads as follows: τά τε 'Ομήρου έξ υποβολής γέγραφε (i. e. Σόλων), ραψωδείσθαι, οίον όπου ό πρώτος έληξεν, εκείθεν άρχεσθαι τὸν έχόμενον. μάλλον οὖν Σόλων "Ομηρον ἐφώτισεν ἡ Πεισίστρατος, ως φησι Διευχίδας έν πέμπτφ Μεγαρικών. It is obviously impossible to determine the exact nature of the services of Pisistratus to Homer as indicated by the word "ἐφώτισεν." Even the very reading of the text itself after the word "Πεισίστρατος" has been questioned by scholars, not, however, because the manuscript is corrupt, but merely because the sequence of the next sentence is deemed too abrupt. Düntzer (ibid., p. 8), with Ritschl and Lehrs, finds himself compelled to indicate a lacuna after that word. Two insertions into the text have accordingly been proposed, one by Düntzer himself and the other by Ritschl, both being relative clauses descriptive of the literary activity of Pisistratus. That the reputed collection of poems by Pisistratus can find no support in this reference to Dieuchidas has already been pointed out by

<sup>4</sup> Hom. Textkritik, p. 13.

<sup>&</sup>lt;sup>5</sup> Hom. Abhandlungen, p. 5.

<sup>6</sup> Hom. Untersuchungen, p. 241.

Lang.<sup>7</sup> It does show, however, that Diogenes Laertius found a statement in Dieuchidas expressive of his belief in some service performed by Pisistratus for Homer.

So far, the cited passages which attest a mere literary dabbling on the part of Pisistratus have been rather unsatisfactory; they are, briefly, a reference by Strabo to a mere tradition which ascribed the insertion of a line either to Solon or Pisistratus; second, the insertion by Pisistratus of another line in another place according to Plutarch, who is quoting from a writer about whose date we know only this, that, appearing in Plutarch, he must have written earlier than the year 80 A. D., which approximately marks the date of Plutarch's activity; third and last, the statement of Dieuchidas, as quoted by Diogenes Laertius, saying that Solon did more to elucidate Homer (if that is the best way to translate èφώτισεν) than did Pisistratus.

Next, let us consider a few passages in authorities of the time of Cicero and later, who make definite statements about what might with fairness be called a Pisistratean edition of Homer. The earliest reference of this sort in any Latin author occurs in the De Oratore III, 137, where Cicero says with reference to Pisistratus: qui primus Homeri libros, confusos antea, sic disposuisse dicitur ut nunc habemus. The use of the word "dicitur" in this place is significant, showing, as it does, that Cicero is careful not to make the statement on his own authority, but introduces the story as one commonly believed in his own day or as transmitted by previous writers. It is reasonable to suppose that Cicero is indebted for his information on this point either to the Alexandrian scholars, or to some of the philosophers of Greece, or to the rhetoricians of the school of Pergamos, though such a statement is of course merely conjectural.

More definite information about the edition of Pisistratus is preserved to us in the scholia s of the Townley manuscript at the beginning of Book K of the Iliad. It runs thus: φασὶ τὴν ραψωδίαν ὑψ' Ὁμήρου ἰδία τετάχθαι καὶ μὴ εἶναι μέρος τῆς Ἰλιάδος, ὑπὸ δὲ Πεισιστράτου τετάχθαι εἶς τὴν ποίησιν. This scholion is one of our most important bits of evidence and must be carefully considered. First we must note that no literary forgery on the part of Pisistratus is implied, but merely the assigning of a place in the Iliad to a poem which had been separately composed by Homer. Since the insertion of an entire book is a fundamental change to make in any piece of literary work, I think I am justified in considering this passage as pointing in the direction of an entire recension of Homer by Pisistratus. The use of the word "φασί" in this

<sup>&</sup>lt;sup>7</sup> Homer and his Age, London, 1906, p. 46.

<sup>&</sup>lt;sup>8</sup> Ed. Maass, Ox. 1887, p. 341.

passage does not bring to the "source hunter" the despair which is usually attendant on such expressions, because, in this case, it is possible with some degree of accuracy to determine the sources of the Townley scholia. Let us briefly consider this point. The codex Venetus A of the Iliad has the following subscription: παράκειται τὰ ἀριστονίκου σημεία καὶ τὰ Διδύμου περὶ τῆς ᾿Αρισταρχείου διορθώσεως, τινὰ δὲ καὶ ἐκ τῆς Ίλιακης προσωδίας Ήρωδιανου καὶ έκ των Νικάνορος περὶ στιγμης. The clates of these four men are as follows: Aristonicus, 66 B. C.-19 A. D., Didymus in the time of Augustus, Herodian under Marcus Aurelius, and Nicanor probably under Hadrian. Of their connection with the Townlev scholia W. Christ 9 says that to "extracts from the works of these men the scholia of our manuscripts go back. Such are best preserved to us in Venetus, 454 (A); next in worth stand the Townley scholia. . . . To the works of these men there were added in later times also scholia from other grammarians, and especially from the Zητήματα of Porphyrius." Without doubt, therefore, our Townley scholia rest on really ancient authorities and have the same source as the scholia of Venetus A. Jebb 10 also agrees with Christ in deeming Aristonicus, Didymus, Herodian, and Nicanor, together with Porphyrius, the sources of our scholia.11

A clear and valuable reference to the collection of the Homeric poems by Pisistratus or his associates is to be found in Pausanias (VII, 26, 6). When speaking of a certain city in Greece named Δονοῦσσα, he makes the remark: μνημονεύειν δὲ καὶ "Ομηρον ἐν καταλόγφ τῶν σὰν ᾿Αγαμέμνονί φασιν αὐτῆς ποιήσαντα ἔπος,

Οί θ' Υπερησίην τε και αιπεινήν Δονόεσσαν,

Πεισίστρατον δέ, ἡνίκα ἔπη τὰ 'Ομήρου διεσπασμένα τε καὶ ἄλλα ἀλλαχοῦ μνημονευόμενα ἡθροίζετο, ἡ αὐτὸν Πεισίστρατον, ἡ τῶν τινα έταίρων μεταποιῆσαι τὸ ὅνομα ὑπὸ ἀγνοίας. The word "ἡθροίζετο" in this passage must clearly refer to a writing down of the poems or to the collection of such portions as may have existed in writing before the time of Pisistratus. It is furthermore interesting to note that Pausanias is the earliest extant writer to mention anything like a school of revisors and collectors associated with Pisistratus. Later we shall have other and more detailed references to such a body of coworkers.

<sup>9</sup> Griesch. Lit. Gesch., ed. iv, Munich, 1905, p. 71.

<sup>10</sup> Homer, Glasgow, 1887, p. 100.

<sup>11</sup> It is obviously dangerous as well as unnecessary for our present purposes to make any one of these four or five authorities the ultimate source of this scholion. That is a point which cannot be definitely settled. Sufficient it is if I have merely hinted at the real antiquity and trustworthiness of our Townley scholia.

As alone and unassisted in a similar literary undertaking, Pisistratus is described by Aelian (XIII, 14): ὕστερον δὲ (i. e., after Lycurgus, who had just been mentioned) Πεισίστρατος συναγαγὼν ἀπέφηνε τὴν Ἰλιάδα καὶ Ὀδύσσειαν. The word "ἀπέφηνε" without a context might be of doubtful significance, but when, as here, it is combined with "συναγαγὼν," a word which can refer to nothing but a written collection, there can be little doubt that it means "publish" in the modern sense of the word. It should be noted, however, that nothing of the nature of a critical edition is here implied, merely a published collection.

In a seventh 12 century scholion 13 to the Γραμματική of Dionysius Thrax we have the following account of a Pisistratean school, which though interesting is not without obvious historical inaccuracies. It runs thus: ἐκήρυξεν ἐν πάση τῆ Ἑλλάδι τὸν ἔχοντα Όμηρικοὺς στίχους ἀγαγεῖν προς αὐτον . . . καὶ μετὰ τὸ πάντας συναγαγείν, παρεκάλεσεν έβδομήκοντα δύο γραμματικούς συνθείναι τὰ τοῦ 'Ομήρου εκαστον κατ' ιδίαν, ὅπως αν δόξη τῷ συντιθέντι καλως έχειν . . . καὶ μετὰ τὸ έκαστον συνθείναι κατὰ τὴν έαυτοῦ γνώμην, είς εν συνήγαγε πάντας τοὺς προλεχθέντας γραμματικούς. . . . οὖτοι οὖν ἀκροασάμενοι οὐ πρὸς ἔριν, ἀλλὰ πρὸς τὸ ἀληθὲς καὶ πᾶν τὸ τῆ τέχνη ἁρμόζον, ἔκριναν πάντες κοινή και δμοφώνως, κρατήσαι την σύνθεσίν τε και διόρθωσιν 'Αυιστάρχου καὶ Ζηνοδότου. καὶ πάλιν ἔκριναν τῶν δύο συνθέσεών τε καὶ διορθώσεων βελτίονα τὴν ᾿Αριστάρχου. We shall later consider the glaring falsity of this last statement about Aristarchus and Zenodotus when we find a similar statement ridiculed by Tzetzes of the twelfth century. The same scholia likewise contain an epigram on Pisistratus, which, as its date has never been determined, loses much of its importance for our present investigation. The following is an extract:

τον μέγαν έν βουλ $\hat{\eta}$  Πεισίστρατον, δε τον Όμηρον ήθροισα σποράδην το πριν άειδόμενον.

Suidas <sup>14</sup> also, the lexicographer, under the word "σομηρος," relates the story of the collection of poems made by Pisistratus. His words are these: ὕστερον δὲ συνετέθη καὶ συνετάχθη ὑπὸ πολλῶν, καὶ μάλιστα ὑπὸ Πεισιστράτου, τοῦ τῶν ᾿Αθηναίων τυράννου. For this statement Suidas may very well have had Pausanias as his authority. This is not unlikely, inasmuch as the two accounts are substantially similar, that is, in both Pisistratus was only one of several who collected the Iliad and Odyssey.

<sup>12</sup> The principal commentators on Dionysius Thrax wrote in the sixth and seventh centuries. We probably have here a note by Heliodorus, who wrote in the seventh century, though we cannot determine with certainty the author of this scholion.

<sup>13</sup> In Bekker's Anecdota, p. 767 ff.14 Ed. Bernhardy, Halle, 1853, 2, 1096.

By the use of the expression  $i\pi\dot{o}$   $\pi\dot{o}\lambda\lambda\hat{\omega}\nu$  Suidas rather implies different collections separated by considerable lapses of time, so that it seems to me very possible that, as Lachmann <sup>15</sup> suggests, he may have misinterpreted his sources, misunderstanding a reference to the different collectors of the Pisistratean school as an allusion to compilers among the predecessors of Pisistratus.

Coming now to Tzetzes, a commentator of the twelfth century, we find that at one time in his life he believed in a collection of Homer by a Pisistratean school of seventy-two, though, as will appear later. he subsequently rejected this theory, expressing the greatest disgust with Heliodorus, 16 whom he had used as his authority. His first belief he expresses in the following words: 17 Πεισίστρατος δε ό φιλολογώτατος, έν χρόνοις τοῦ Σόλωνος τυραννήσας έν ταις Αθήναις, κήρυγμα έξεκήρυξε τὸν έχοντα έπη Όμηρου, αποκομίζειν αὐτὰ πρὸς αὐτόν, καὶ εκαστον έπους χρυσοῦν αντιφορτίζεσθαι νόμισμα. οῦτω δὲ συναγείρας αὐτά, εβδομήκοντα καὶ δύο γραμματικοις ένι έκάστω επέδωκε κατ' ιδίαν τεθεωρικέναι και συνθείναι αυτά : έκείνος δέ την ένδς έκάστου αὐτῶν σύνθεσιν ἀπεγράφετο. ὕστερον δὲ δμοῦ πάντας συναγαγών πιιρακλήσεσι, μεγάλαις τε δωρεαίς έκείνους δεξιωσάμενος, υπέδειξε την ιδπογραφήν της ένος έκαστου συνθήκης, και ηξίωσεν αυτούς φιλαλήθως και αφιλέχθρως είπειν. ότου άρα είη κρείττων ή σύνθεσις και πάντες την 'Αριστάρχου και Ζηνοδώτου ύπερεξέκριναν, έκ δυείν δὲ πάλιν, τὴν Αριστάρχειον, καθ' ἡν νῦν τὸ παρὸν τοῦ Ὁμήρου Βιβλίον συντέθειται. Evidently, at some later time, Tzetzes got new light on this subject, and realizing the absurdity of making the Alexandrian Aristarchus and Zenodotus the contemporaries of Pisistratus, and boiling with indignation when he reflected how he had been taken in, thus expressed his new belief, prefacing it with a brief note in which he makes poor Heliodorus the scapegoat of his disgust by the amusing epithet of opprobrium τῶ βδελυρῷ. The passage runs thus: Πεισθεὶς 18 Ήλιοδώρω τῷ βδελυρῷ εἶπον συνθεῖναι τὸν "Ομηρον ἐπὶ Πεισιστράτου εβδομήκοντα δύο σοφούς, ὧν έβδομήκοντα δύο είναι καὶ τὸν Ζηνόδοτον καὶ τὸν ᾿Αρίσταργον. καίτοι τεσσάρων ανδρών έπὶ Πεισιστράτου συνθέντων τον "Ομηρον, οῖτινές είσιν οὖτοι ' ἐπικόγκυλος, 'Ονομάκριτος 'Αθηναίος, Ζώπυρος 'Ηρακλεώτης καὶ 'Ορφεύς Κροτωνιάτης. This last statement I have found in no author before Tzetzes, so that I am at a loss to know his authority. In this passage the expression έπὶ Πεισιστράτου could be interpreted as meaning

<sup>15</sup> Betrachtung ü, Homers Ilias, Berlin, 1847, p. 32.

<sup>&</sup>lt;sup>16</sup> This fact serves to strengthen my belief that Heliodorus was the composer of the cited scholion to Dionysius Thrax, since there he expounds at length the story of the school of seventy-two.

<sup>17</sup> Exegesis to Iliad, ed. G. Hermann. Leip., 1812, p. 45, 1. 27.

<sup>18</sup> See Ritschl's Opuscula, I, 205, which contain Tzetzes' Prolegomena to the scholia of Aristophanes. The word printed as ἐπικόγκυλος has been variously emended, but the MSS, are hopelessly defective at this point.

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merely that "in the time of Pisistratus" this collection of Homer took place, did not Tzetzes elsewhere give us a more definite statement of his opinion. On page 207 of his prolegomena to the scholia of Aristophanes we find these words: τὰς Ὁμηρείους δὲ κατεξαίρετον πρὸ διακοσίων καὶ πλειόνων ἐνιαυτῶν Πτολεμαίου τοῦ Φιλαδέλφου καὶ τῆς διορθώσεως Ζηνοδότου συντέθεικεν σπουδῆ Πεισίστρατος παρὰ τῶν τεσσάρων τούτων σοφῶν ἐπὶ Κογκύλου, "Ονομακρίτου τε 'Αθηναίου. Ζωπίρου τε 'Ηρακλεώτου καὶ Κροτωνιάτου 'Ορφέως, Οὕτω μὲν ἐν χρόνοις τοῦ Πεισιστράτου τοῖς τέσσαρσι τουτοις σοφοῖς αἱ 'Ομηρικαὶ συγγραφαὶ τεμαχίοις περιφερόμεναι συνετέθησαν καὶ βίβλοι ἐγένοντο. Hence we see that Tzetzes regarded Pisistratus as an active participant in the work of collection, though he was assisted by these four men.

There can be little doubt, I think, that for these prolegomena he was drawing on the ancient scholia. John Williams White, 19 in speaking of Tzetzes' interlinear notes to the Aves in codex Urbinas, says: "He was writing a brief commentary on the Aves based on the old scholia with additions 'by the editor.'" By some scholars, however, Tzetzes is held in very low esteem as an authority. For example, Sandys 20 says of him: "His inordinate self-esteem is only exceeded by his extraordinary carelessness. He calls Simonides of Amorgus the son of Amorgus, makes Naxos a town in Euboea, describes Servius Tullius as 'consul' and 'emperor' of Rome, and confounds the Euphrates with the Nile. He is proud of his rapid pen and remarkable memory; but his memory often plays him false, and he is for the most part dull as a writer and untrustworthy as an authority." With regard to the passage already quoted from Tzetzes, Monro 21 writes: "Everything points to the conclusion that the story is a mere fabrication. He does not give his authority, and it can scarcely be imagined that he had access to sources unknown to the generality of Byzantine scholars." But is not this unjustly making light of the character of Tzetzes? The worst that Sandys cares to say about him is that he was careless; but is it carelessness that gives birth to such a circumstantial statement as this? I cannot see how such a detailed story could have come full-grown like Minerva from the head of any writer unless his fault had been something much more serious than carelessness; but this no one would say of Tzetzes. I prefer then to follow Mr. White in believing Tzetzes to have based his prolegomena on the old scholia with some additions, and accordingly I think it most probable that for this statement he must have found some authority in the scholia.

<sup>19</sup> Harvard Studies, XII, 104.

<sup>20</sup> Hist. of Class. Scholarship, ed. ii, 419.

<sup>21</sup> Od., XIII-XXIV, ed. i, Ox., 1901, p. 406.

Let us now briefly consider references to any of these four associates of Pisistratus in literature earlier than the time of Tzetzes. In Herodotus (VII, 6) these words are applied to Onomacritus: ἄνδρα ᾿Αθηναίον χρησμολόγον τε καὶ διαθέτην χρησμῶν τῶν Μουσαίου . . . ἐξηλάθη γὰρ ὑπὸ Ίππάρχου τοῦ Πεισιστράτου ὁ Ὀνομάκριτος ἐξ ᾿Αθηνέων. As a contemporary of Hipparchus, so, without doubt, he was also a contemporary of Pisistratus. Thus Herodotus vouches for the chronology of Tzetzes so far as Onomacritus is concerned. But we must admit that in all probability the connection of Onomacritus with Pisistratus in the Homeric collection was unknown to Herodotus; hence his silence in this place. The only other of these four men to whom I have been able to find a reference in an ancient author is Orpheus, -not the great Orpheus, but one of Croton, who is referred to by Suidas (p. 1176). under the words 'Ορφεύς Κροτωνιάτης in the following manner: ἐποποιός, ον Πεισιστράτω συνείναι τω τυράννω 'Ασκληπιάδης Φησίν έν τω εκτω βιβλίω των Γραμματικών. This writer Asclepiades was, according to Sandys (p. 160), a native of Myrleia in Bithynia, and was born at some period between 130 and 180 B. c. As Orpheus was an epic poet and associated with the tyrant Pisistratus, according to Asclepiades, I think we are justified in inferring that the connection was doubtless of a literary nature. This fact, of course, is not enough to vindicate the whole story of Tzetzes, but it shows that in the case of at least one of these four men, his connection with Pisistratus was known even before the beginning of our era, and that in this one regard the so-called fabrication of Tzetzes shows a remarkable coincidence with the truth.

In the commentary of Eustathius on the Iliad and Odyssey, written about the year 1175 of our era, and shortly after the time of Tzetzes, are found two different accounts of the Pisistratean collection, obviously drawn from different sources. In the first, we are surprised to find him giving credence to the story we have met before of the Pisistratean school dominated by Aristarchus and Zenodotus. In the second, Pisistratus himself is mentioned as sole author of a probable recension. The passages are as follows, first from his commentary to the first book of the Iliad (p. 5, l. 28): οί δὲ συνθέμενοι ταύτην (i. e. Ἰλιάδα), κατ' ἐπιταγὴν, ως φασι. Πεισιστράτου τοῦ των 'Αθηναίων τυράννου, γραμματικοί καὶ διορθωσάμενοι κατὰ τὸ ἐκείνοις ἀρέσκον, ὧν κορυφαίος 'Αρίσταρχος καὶ μετ' ἐκείνον Ζηνόδοτος διὰ τὸ ἐπίμηκες καὶ δυσεξίτητον καὶ διατοῦτο προσκορὲς κατέτεμον αὐτὸ εἰς πολλά. This undoubtedly refers to a Pisistratean collection, but not one in which Pisistratus took a personal part. The second of these passages (Vol. II, p. 309, l. 17) is identical in meaning with the Townley scholion already quoted, and almost identical in form. The source of both is doubtless the same: Φασὶ δὲ οἱ παλαιοὶ τὴν ραψωδίαν ταύτην ὑΦ' 'Ομήρου

ίδία τετάχθαι καὶ μὴ ἐγκαταλεγῆναι τοῖς μέρεσι τῆς Ἰλιάδος, ὑπὸ δὲ Πεισιστράτου τετάχθαι εἰς τὴν ποίησιν.

It is necessary, I think, at this point to consider briefly from what authorities Eustathius drew his information. Düntzer 22 seems agnostic on this point, though confident in the real antiquity of such sources. "It is difficult," he writes, "to see whom Eustathius means by οί παλαιοί in his note on the beginning of Iliad K. We cannot say that he means any particular scholar of the Alexandrian school. the other hand, much less can we say that the supposition of the insertion of a book by Pisistratus was wholly unknown to the Alexandrians. So the supposition of Lehrs, that the old Alexandrines had no knowledge of the especial critical significance of the arrangement of the Homeric poems by Pisistratus, is unfounded." Eustathius, as we know,23 further used as sources an epitome made from the commentaries of the four men whom I have previously mentioned as probable sources of our Townley scholia, viz., Aristonicus, Didymus, Herodian, and Nicanor. Likewise the Λέξεις of Aristophanes, the rhetorical dictionary of Dionysius, the encyclopaedic lexicon of Apion, and Herodorus and the Paralipomena of Porphyrius. Furthermore, I have noted at least one place in Eustathius (Vol. I, p. 230, l. 46) where he quotes directly from Strabo (IX, 394, 10) in very nearly his exact words, Σόλων δὲ ἡ Πεισίστρατος παρενέγραψεν ένταῦθα μετὰ τὸν Ομήρου στίχον τὸ,

## στησε δ' άγων, ζυ' 'Αθηναίων ζσταντο φάλαγγες

καὶ οἴτω μάρτυρι τῷ ποιητῆ ἐχρήσατο τοῦ τὴν νῆσον ἐξ ἀρχῆς ᾿Αθηναίων ὑπάρξαι, ὡς ὁ γεωγράφος ἱστορεῖ. And finally Sengebusch,<sup>24</sup> who refers in turn to the opinion of Lehrs, holds exactly the same view as Christ. Important therefore are the statements of Eustathius, inasmuch as he himself, though a comparatively late writer, drew his information, so far as we can ascertain, from writers even as early as the Alexandrian school.

In a document three centuries later than Eustathius, that is, in a fifteenth century manuscript in the library of the Collegio Romano, containing fifteen plays of Plautus, is preserved a version of the Pisistratean story identical with the account of Tzetzes. Ritschl conjectures that these scholia are drawn from Tzetzes, as they are, without a doubt. The similarity is conclusive. Towards the end of the Poenulus they run

<sup>&</sup>lt;sup>22</sup> Hom. Abhandlungen, Leip., 1872, p. 4.

<sup>23</sup> See Christ, Griesch. lit. Gesch., ed. iv, p. 72.

<sup>&</sup>lt;sup>24</sup> Homerica Dissertatio, I, Leip., 1870, p. 40.

thus: 25 Ceterum Pisistratus sparsam prius Homeri poesim ante Ptolemaeum Philadelphum annis ducentis et eo etiam amplius sollerti cura in ea quae nunc extant redegit volumina, usus ad hoc opus divinum industria quattuor celeberrimorum et eruditissimorum hominum, videlicet, Concyli, Onomacriti Athenien. Zopyri Heracleotae et Orphei Crotoniatae. Nam carptim prius Homerus et non nisi difficillime legebatur. This of course is a quotation from the passage of Tzetzes written after he had revolted from Heliodorus and his belief in the school of seventy-two grammarians. These scholia also contain a few sentences adapted from the Prolegomena of Tzetzes in the place where he applies to Heliodorus the epithet of τῷ βδελυρῷ. They read as follows: Quum etiam post Pisistrati curam et Ptolemaei diligentiam Aristarchus adhuc exactius in Homeri elimandum collectionem vigilavit. Heliodorus multa aliter nugatur quae longo convitio Cecius reprehendit. Nam ol' LXXII duobus doctis viris a Pisistrato huic negotio praepositis dicit Homerum ita fuisse compositum. Qui quidem Zenodoti et Aristarchi industria omnibus praelatam comprobariut, quod constat fuisse falsissimum. Quippe cum inter Pisistratum et Zenodotum fuerint anni supra ducentos. Aristarchus autem quattuor annis minor fuerit ipso et Zenodoto atque Ptolemaeo. This shows better than anything else the utter falsity of the account given in Bekker's Anecdota (p. 767 ff.). By the clause "Quum etiam post Pisistrati, etc." the text recension of Zenodotus and Aristarchus is unquestionably meant. But these are not quoted as the words of Tzetzes 26 but of Heliodorus, as the "multa aliter" clearly indicates. Without doubt, "Nam ol' LXXII, etc.," down to "comprobarint" comes from Heliodorus, and "quod constat" to the end from Tzetzes. But these late scholia add no new testimony to that already given by Tzetzes himself.

Our last and probably latest reference to the collection of Homeric poems by Pisistratus is found in two lives <sup>27</sup> of Homer which were made from the collation of facts preserved in fourteenth and fifteenth century manuscripts. A passage from one of them reads: περιιών δὲ τὰς πόλεις ἦδε [[Ομηρος] τὰ ποιήματα. Εστερον δὲ Πεισίστρατος αὐτὰ συνήγαγεν, ὡς τὸ ἐπίγραμμα τούτου δηλοῖ

τὸν μέγαν ἐν βουλαῖς Πεισίστρατον, δς τὸν "Ομηρον ήθροισα σποράδην τὸ πρὶν ἀειδόμενον.

<sup>&</sup>lt;sup>25</sup> These scholia were first published by F. W. Ritschl, and can be found in Vol. I of his Opuscula, p. 6, or in his Alexandrinische Bibliotheken, Breslau, 1838, p. 4.

<sup>26</sup> See Ritschl, Op., I, 33.

<sup>27</sup> See Jahn's Neue Jahrb. für Philologie u. Paedagogik, 9es Suppbd., p. 508.

Briefly summing up the testimony of such accounts as we may consider reliable for an Homeric edition by Pisistratus or Pisistratus and his associates, the result is as follows. The accounts in Cicero, the Townley scholia, Aelian, Suidas, and Eustathius all point to a collection of the poems by Pisistratus alone and unassisted. The accounts in Pausanias, Tzetzes, and, of course, the scholia to Plautus, are the only ones which indicate any kind of a Pisistratean school. I do not think, however, that we ought to consider this as strong evidence that Pisistratus was not assisted by a board of associates in his work of collecting. Naturally if he, a ruler in absolute authority and eager for fame in letters, chose to be the proud supervisor of such a literary undertaking, even though his co-workers were ever so numerous, the edition which was produced would be called by subsequent writers "Pisistratus's Edition" and the "Collection which Pisistratus made," while his helpers would be gradually disregarded, just as we, for instance, refer to our Bible as "King James's Version."

The fact that the story of a collection of Homeric poems by Pisistratus, or Pisistratus and certain associates, was known by Cicero and several reputable writers after him is very significant. No one would presume to say that, as in the case of Tzetzes, so also in the case of Cicero, this story is a fabrication. In fact, he himself uses the word "dicitur," which we may translate "we are told." What, then, was his authority and the authority of these subsequent writers? It seems at least probable that the Alexandrian School, for instance, must have played a part in handing down the tradition. The most that can be said against this is that neither Aristarchus nor any of his successors in any of their writings which are extant in whole or in part mention the connection of Pisistratus with Homer as a collector or reviser; but this is obviously an unfair objection because, without doubt, only small portions of all their writings have come down to us. And yet Flach 28 derives especial satisfaction from the contemplation of such facts as, for instance, that Aristarchus never so much as implies that the insertions into the text of Homer especially complimentary to the Athenians were found only in the manuscripts that came from Athens, although, if this were the state of things, we should expect him to mention it.

<sup>&</sup>lt;sup>28</sup> Peisistratus u. seine Lit. Tätigkeit, Tübingen, 1885, p. 39.

As to whether Homer had existed in writing before the time of Pisistratus or not, that is not so important a question, and with regard to it only general inferences can be drawn from the statements of the ancients themselves. The testimony of Pausanias 29 and the first 30 and second 31 lives of Homer tend to show that until the time of Pisistratus, at least, oral tradition was the medium of transmission. Cicero, 32 however, the Townley scholia, 33 and Suidas 34 give evidence which is more definite and points directly to a written tradition. evidence then is quite fairly divided; but on the whole I feel safer in favoring a written Iliad and Odyssey before the days of Pisistratus, since the tradition recorded by Cicero is likely to have been older and more reliable than the one mentioned by Pausanias, and especially because the Townley scholia ought to outweigh any evidence contained in the lines of Homer based merely on manuscripts which are themselves inferior to the Townley. Furthermore, in addition to Suidas, there are several other authors whose testimony in favor of a written Homer before Pisistratus is sure. Plutarch says in his life of Lycurgus,35 when referring to the state of the Homeric poems in Greece in the time of the great lawgiver [οί "Ελληνες] ἐκέκτηντο δὲ οὐ πολλοὶ μέρη τινά [τοῦ 'Ομήρου], where it seems that a word like ἐκέκτηντο must refer to a tangible written copy. Aelian also (XIII, 14) in speaking of Lycurgus writes: πρώτος ές την Ελλάδα έκόμισε την Ομήρου ποίησιν. Here again the supposition of a manuscript seems imperative. Plutarch likewise. in his life of Solon (X, 1), referring to his insertion of a verse, says: έμβαλόντα γὰρ αὐτὸν ἔπος εἰς νεῶν κατάλογον ἐπὶ τῆς δίκης ἀναγνῶναι, where this last word cannot leave us in a moment's doubt. Here dikng refers to the trial in which the Lacedaemonians were made arbiters between the Athenians and Megarians. Diogenes Laertius (1, 2, 48), with reference to this same performance of Solon's, uses the word έγγράψαι, prefacing it however by ἔνιοι δέ φασιν. I therefore cannot agree with these words of Bonitz, 36 "that this was the first time that the whole of the poems was written down may be clearly inferred from the form and character of the numerous statements in regard to it." Christ and Jebb, both on grounds other than I have taken, favor the theory of a written trans-

<sup>29</sup> Poems said to have been μνημονευόμενα.

<sup>30 [&</sup>quot;Ομηρος]  $\hat{\eta}$ δε τὰ ποιήματα.

<sup>31</sup> Poems said to have been πρότερον άδόμενα.

<sup>32 &</sup>quot;Libros" of Homer referred to.

<sup>33</sup> Η. Κ said to have been τετάχθαι ύφ' 'Ομήρου.

<sup>34</sup> έγραφε "Ομηρος.

<sup>35</sup> Plutarch I, p. 82, I. 9, ed. Sintenis, Leip., 1884.

<sup>&</sup>lt;sup>36</sup> Origin of Homeric Poems, N. Y., 1880, p. 27.

mission. Jebb 37 is of the opinion that "it cannot be proved that the Homeric poems were not committed to writing either when originally composed or soon afterwards. For centuries they were known to the Greek world at large chiefly through the mouth of rhapsodes. But that fact is not inconsistent with the fact that the rhapsodes possessed written copies. On the other hand, a purely oral transmission is hardly The judgment of Christ (p. 65) is thus expressed: conceivable." "Fully one hundred years before the Athenian Tyrants, the Ionic books were reduced to writing, and it would truly be strange if the honor of a written copy should have fallen to the lot of an iambic or elegiac poet sooner than to the great national poet. Also the testimony shows that Pisistratus made nothing more than a complete Iliad and Odyssey. Probably before that time certain parts had been reduced to writing to aid the memory, as, for example, the Catalogue of Ships."

Perhaps at this point it would not be out of place to make a brief excursus on stories which, for the most part, without mentioning the name of Pisistratus, tell us of other men who are reported to have done work of some kind in connection with the Homeric poems. making this excursus a chronological arrangement of evidence by authors (the system I have adopted up to this point) does not seem necessary or even advisable inasmuch as it would cause confusion through the separation of all passages by different authors, though referring to the same historical personage, I have thought it best to arrange the following passages in the chronological order of the different persons whose activity is described therein. In La Roche's Homerische Textkritik im Altertum (p. 7) there is published an interesting fragment of Heraclides who lived at about the middle of the second century B. C. Λυκουργος έν Σάμω έτελεύτησε καὶ τὴν Ομήρου ποίησιν παρὰ τῶν ἀπογόνων Κρεωφύλου λαβών πρῶτος διεκόμισεν εἰς Πελοπόννησον. This, of course, is another story entirely, and, even if true, is nothing to influence our belief in the nature of the services that Pisistratus may have performed for Homer at a much later date. 38 Similar also is a statement made about Lycurgus by a much later writer in the second half of the first century A. D. Plutarch (Vol. I, p. 82, l. 2) tells how Lycurgus, when he was in Asia, realizing that the Homeric poems contained educational elements as well as political qualities, determined to bring them to Athens. Then comes the significant part: η γάρ τις ήδη δόξα των έπων αμαυρά παρά τοις Ελλησιν, έκέκτηντο δε ου πολλοί μέρη

<sup>37</sup> Homer, Boston, 1887, p. 114.

 $<sup>^{38}</sup>$  This fragment is additional evidence for a written Homer before the days of Pisistratus.

τινά, σποράδην τῆς ποιήσεως, ὡς ἔτυχε, διαφερομένης. γνωρίμην δὲ αὐτὴν καὶ μάλιστα πρῶτος ἐποίησε Λυκοῦργος. This again is interesting as throwing light on the life of Lycurgus and the early history of the Homeric poems, though it is not of a nature to influence our judgment as to the truth or falsity of the Pisistratean story. And lastly Aelian (XIII, 14) makes substantially the same statement about Lycurgus when he writes: ἀψὲ δὲ Λυκοῦργος ὁ Λακεδαιμόνιος ἀθρόαν πρῶτος ἐς τὴν Ἑλλάδα ἐκόμισε τὴν 'Ομήρου ποίησιν. So much for Lycurgus.

We have already seen that the insertion of verse 558 of Iliad B was said by Strabo to have been ascribed by one tradition to Pisistratus and by another to Solon. To this I can add two accounts by somewhat later writers who, from hearsay or report, make Solon the author of the same interpolation without any mention of Pisistratus. The first of these is from Plutarch's life of Solon (X, 1): οὐ μὴν ἀλλὰ τῶν Μεγαρέων ἐπιμενόντων πολλά κακά καὶ δρώντες ἐν τῷ πολέμῳ καὶ πάσχοντες ἐποιήσαντο Λακεδαιμονίους διαλλακτάς καὶ δικαστάς. Οἱ μὲν οὖν πολλοὶ τῶ Σόλωνι συναγωνίσασθαι λέγουσι την 'Ομήρου δόξαν ' έμβαλόντα γάρ αὐτὸν ἔπος εἰς νεῶν κατάλογον ἐπὶ τῆς δίκης ἀναγνῶναι, — then follow verses 557 and 558 of Iliad B. Diogenes Laertius (1, 2, 48) also writes with regard to Solon: ένιοι δέ φασι καὶ έγγράψαι αὐτὸν εἰς τὸν κατάλογον τοῦ Όμήρου μετὰ τὸν (v. 557. v. 558). And, to end the discussion of Solon, we have in Diogenes Laertius still another passage already quoted (1, 57) which bears testimony merely to a certain literary activity in connection with Homer on the part of Solon, earlier of course than the time of Pisistratus. In a certain respect, expressed by έφωτισεν, according to Dieuchidas the Megarian, Solon is said to have surpassed Pisistratus: τά τε Ομήρου έξ υποβολής γέγραφε ραψωδείσθαι, οδον οπου ο πρώτος έληξεν, έκειθεν ἄρχεσθαι τὸν ἐχόμενον. μᾶλλον οὖν Σόλων Ομηρον ἐφώτισεν ἡ Πεισίστρατος, ως φησι Διευχίδας έν πέμπτω Μεγαρικών.

Hipparchus, the elder of the sons of Pisistratus, is the only other man to whom I have found activity in connection with the Homeric poems ascribed. In one account he is said to have brought them to Greece, in the other, to Athens, and in both to have ordered the rhapsodes to sing them at the Panathenaic festival. The first account, contained in the pseudo-Platonic dialogue Hipparchus (228 B) runs as follows: Ἱππάρχφ, δε τῶν Πεισιστράτον παίδων ἦν πρεσβύτατος καὶ σοφώτατος, ὅς ἄλλα τε πολλὰ καὶ καλὰ ἔργα σοφίας ἀπεδείξατο, καὶ τὰ ὑμήρον ἔπη πρῶτος ἐκόμισεν εἰς τὴν γῆν ταυτηνί, καὶ ἢνάγκασε τοὺς ῥαψφιδοὺς Παναθηναίοις ἐξ ὑπολήψεως ἐφεξῆς αὐτὰ διιέναι. ὥσπερ νῦν ἔτι οἴδε ποιοῦσιν. Now the question whether Plato or somebody else wrote the dialogue which contains this information is not essential to this investigation. But it is necessary for us to ascertain as nearly as may be when it was writ-

ten, and something, if possible, about the writer. Accordingly a slight digression on its authenticity will not be out of place.

That the genuineness of this dialogue was doubted, even in antiquity, has been maintained by some, notably Wolf, on the authority of the following passage in Aelian (VIII, 2): οὐκ ὥετο γὰρ δεῖν οὐδενὶ φθονεῖν σοφίας, ᾶτε ὧν καλὸς καὶ ἀγαθός. λέγει δὲ Πλάτων ταῦτα, εἰ δὴ ὁ Ἦπαρχος Πλάτωνός ἐστι τῷ ὄντι. But this contains, at the very end, as Grote 39 points out, a conjectural emendation. Hercher in his edition ascribes the reading övil with no following word to the emendation of Perizonius, doubtless in his edition of 1701.40 But the manuscripts read τφ ουτι μαθητής. Grote's contention is that "if you construe the passage as it stands without such conjectural alteration, it does not justify Wolf's inference 'that the genuineness of the Hipparchus was doubted in antiquity." But if we do not emend with Perizonius we have an historical error, the suggestion that Hipparchus might have been the pupil of Plato, a mistake which Mr. Grote probably with perfect justice considers "nowise impossible in the case of Aelian." But if we do not emend, I fail to see the connection of the statement "if Hipparchus is really a pupil of Plato" with the preceding. It is entirely lacking in logical sequence.

There is also another argument, which, so far as I can discover, has not been adduced by any one as yet, but which to me is conclusive in favor of adopting the emendation of Perizonius. Aelian, in the same book, and only a few lines before the disputed passage, has these words (VIII, 2): "Ιππαρχος ο Πεισιστράτου παις πρεσβύτατος ων των Πεισιστράτου καὶ σοφώτατος ἦν ᾿Αθηναίων. οὖτος καὶ τὰ Ὁμήρου ἔπη πρῶτος ἐκόμισεν ἐς τὰς \*Αθήνας, καὶ ἢνάγκασε τοὺς ῥαψωδοὺς τοῖς Πανοθηναίοις αὐτὰ ἄδειν. Now, after a comparison of this with the passage from the Hipparchus (228 B) which I have just quoted, I do not think that there can be any doubt that Aelian was quoting outright from pseudo-Plato. What could be more natural then that a few lines later he should make a reference to the book Hipparchus from which he had just quoted and which was still running in his mind, and probably to our very passage containing the words, ος άλλα τε πολλά και καλά έργα σοφίας ἀπεδείξατο, which would make a very tolerable precedent for Aelian's, — οὐκ ικότο γὰρ δεῖν οὐδενὶ Φθονεῖν σοφίας, ἄτε ὧν καλὸς καὶ ἀγαθός. It therefore seems to me by all means preferable and even necessary to adopt the emendation of Perizonius and to agree with Wolf that the authenticity of the Hipparchus was doubted even as early as Aelian (fl. 130).

Diogenes Lacrtius, who flourished at some time near the beginning

<sup>&</sup>lt;sup>39</sup> Plato, London, 1888, II, 85,

<sup>40</sup> See Christ, p. 762.

of the third century, contains the following very possible reference to the dialogue under consideration and to the man whom he supposed to be the author (2, 122): Σίμων 'Αθηναίος, σκυτοτόμος · οὖτος ἐρχομένου Σωκράτους έπὶ τὸ έργαστήριον καὶ διαλεγομένου τινά, ὧν έμνημόνευεν ὑποσημειώσεις έποιείτο · ὅθεν σκυτικούς αὐτοῦ τοὺς διαλόγους καλοῦσιν. εἰσὶ δὲ τρεῖς καὶ τριάκοντα ἐν ἐνὶ φερόμενοι βιβλίω, — then follows a list of thirty-one titles. among which is the title περὶ φιλοκερδοῦς, which is the subject under diseussion in the pseudo-Platonic Hipparchus. In order to fix the date of this Simon I must quote another passage from Diogenes Laertius' life of Simon (2, 123), which reads as follows: οὖτος, φασί, πρώτος διελέχθη τους λόγους τους Σωκρατικούς, έπαγγειλαμένου δε Περικλέους θρέψειν αυτόν καὶ κελεύοντος απιέναι πρός αὐτόν, οὐκ αν έφη την παρρησίαν αποδόσθαι. then places his sphere of activity in the age of Pericles, making him a little older than Plato himself. Accordingly Boeckh, connecting the Hipparchus and the Minos, as works by the same author (basing his decision on evidences of style, apart from the statement of Diogenes to the same effect), published at Heidelberg in 1810 these two dialogues and two others in a separate edition which he called "Simonis Socratici, ut videtur, dialogi quattuor." Grote, as I have already implied from my previous quotation of his opinion, considers the Hipparchus one of the inferior works of Plato. Steinhart as quoted by Fritzsche 41 dates the composition of the Hipparchus in the Macedonian Age (say from 350-320 B. c.) deducing his opinion from internal evidence. First, Hipparchus is lauded, whereas the murderers fail in the common meed of praise, two things which would be more in accord with the spirit of the Macedonian Age than that of the Periclean, for instance; and secondly, the ratio of gold to silver is mentioned as twelve to one (231 D), facts which he considers significant enough to warrant his conclusion. This, of course, if true, would place its composition slightly after the death of Plato. All testimony, therefore, which can be adduced tends to show that if not by Plato himself it was composed by some author almost contemporaneous with him.

I might mention here again, for the sake of completeness, the reference in Aelian to the literary importation by Hipparchus, but as Aelian's sole authority for this story is doubtless the pseudo-Plato, it really has no important evidence to add.

To summarize, then, briefly, this little excursus, the accounts of Lycurgus given by Heraclides, Plutarch, and Aelian contain absolutely nothing to influence our belief as to the activity of Pisistratus. The only story about Solon which seems to concern Pisistratus at all

<sup>41</sup> Stallbaum, Plato, ed. ii, Leip., 1885, b. II, 304.

is the account of Dieuchidas which, we must remember, is quoted at second hand, and contains those words, μάλλον έφώτισεν κτλ, which seem too vague and doubtful in their significance to be given very much weight. The only account, therefore, which conflicts with the supposition of a Pisistratean edition is contained in the pseudo-Plato. This story I hesitate to reject hastily because of its antiquity. But yet there are several facts in connection with it which we must face: first, the author is doubtful, practically unknown; second, the story is found nowhere else except in Aelian, so far as I can discover; third, it is practically contradictory to the statements I have quoted about Lycurgus, to say nothing of the accounts of Pisistratus, 42 which are based on good authority. How such a plausible story, if true, could have been so nearly forgotten, or how so disregarded by subsequent writers, had the pseudo-Plato possessed a good reputation for historical accuracy, is past understanding. Very plausible is the supposition that it may have been a confusion of two or more stories. This opinion is favored by Flach when he writes (p. 21): "The author of pseudo-Plato was not reliable in comparison with Dieuchidas,43 he makes noticeable historical blunders, and was probably lightly recording some local tradition. This tradition arose from an analogy with Solon and from the fact that Hipparchus was a patron of literature, as shown by his calling over Anacreon from Samos in 522 B C., after the death of Polycrates." On the whole I am forced to admit this rather plausible explanation of the practically unique account in the pseudo-Plato.

Finally, then, what inference are we justified in deducing with regard to the literary activity of Pisistratus in connection with the Homeric poems? We must endeavor to avoid any conclusions which, however plausible, are not fully justified by our evidence. For example, Monro says (p. 406): "The Pisistratean edition is excluded by the account adopted in the pseudo-Platonic Hipparchus, which leaves no room for a collection of Homeric verses." But it is not just that the authority of this one anonymous writing should outweigh all other passages which testify to a collection of Homeric poems by Pisistratus, and are drawn from such reliable sources as Cicero, Aelian, Pausanias, and the scholia of our second best manuscript. Neither can I agree

<sup>42</sup> The only way in which I can reconcile this with the accounts about Pisistratus is by supposing that Hipparchus introduced the Homeric poems into Greece a good many years prior to the death of Pisistratus his father. But this supposition seems rather improbable.

<sup>43</sup> Flach gives no eredence to the stories about Pisistratus, but believes in the greater Homeric activity of Solon. Hence the mention of Dieuchidas, who says Σόλων μᾶλλον ἐφώτισεν κτλ.

with Monro in any such statement as that such a collection "may be shown to be unknown to the Alexandrian grammarians," for their works are preserved to us in such an incomplete state that it is absolutely impossible to say exactly what they did mention and what not. T. W. Allen, in the Classical Review, 44 assuming the reality of this silence, has an explanation which is possible. He writes: "If Pisistratus were the reputed father of the  $\kappa o \nu \dot{\eta}$ , it is natural that we find no mention of him in the scholia. The grammarians ignore the  $\kappa o \nu \dot{\eta}$  because it was in every one's hands, and because it had suffered by transmission. The same account explains the absence of reference to the Athenian edition."

The explanation of the sources of the so-called Pisistratean legend by those who disbelieve in it has afforded critics the exercise of much originality and ingenuity, but it is based for the most part on merest conjecture. Flach (p. 41) is of the opinion that the story of Pisistratus's edition came from Megarian historians of little scientific importance, and was "boomed" by the scholars of the Pergamean school that they might find a great literary man to belittle the Homeric scholars of their rival school, the Alexandrian. Likewise Nutzhorn, 45 who disbelieves in the Pisistratean recension, makes light of the testimony of Cicero, saying that Cicero drags in Pisistratus here merely as an added example of the point he is trying to establish, — how necessary it is for the great statesman to be a learned man as well. However that may be, unless Nutzhorn is willing to admit that Cicero in this place is deliberately falsifying evidence (i. e., the tradition which he cites), I fail to see that his remark has any point. Desire on the part of Cicero to illustrate a principle aptly cannot be said to imply the use of fictitious examples. Interesting also, and more probable, is the conjecture of Düntzer (p. 17), who makes Dicaearchus in his Βίος 'Ελλάδος the authority for the statement of Cicero. This opinion is based on the fact that Dicaearchus was an author of general popularity with Cicero, as shown by his references to him on several occasions, his work being of great importance in the literary history of Greece.

After such a discussion of conjectures we are reminded of the words of Wolf: 46 "Nunc vero nihil opus est coniecturas capere. Historia loquitur. Nam vox totius antiquitatis et, si summam spectes, consentiens fama testatur Pisistratum carmina Homeri primum consignavisse litteris, et in eum ordinem redegisse quo nunc leguntur. Hoc pos-

<sup>44</sup> XV, p. 8 (1901).

<sup>45</sup> Die Entstehungsweise der Hom. Gedichte, Leip., 1869, p. 48.

<sup>46</sup> Prolegomena ad Homerum, ed. ii (posthumous), Berlin, 1876, c. xxxiii.

terius Cicero, Pausanias et reliqui omnes qui mentionem rei faciunt, iisdem prope verbis et ut vulgo notissimum perhibent." At first thought this statement seems too sweeping to be literally true, but when one bears in mind that the only statement by an ancient authority really contradictory to the idea of a Pisistratean edition of Homer is contained in the pseudo-Plato of doubtful authority, and when one remembers that the accounts, even as old as Cicero, were, as is most probable, drawn from much older authorities which are now lost, then one can see that this statement, though framed in bold language, was not made without due deliberation. The statement, "primum consignavisse litteris," however, does not seem to have equal justification. On the contrary, available evidence seems to indicate that even before the time of Pisistratus the Homeric poems, at least large portions of them, already existed in writing.

All our testimony clearly shows, I think, that Pisistratus, who was a  $\tau \dot{\nu} \rho a \nu \nu \sigma s$  interested in literature, with the help, as is most likely, of several poets or literary men of his court, was the first to make a careful collection or edition (though in no sense of the word a critical edition) of the Iliad and Odyssey, on the basis of what scattered written copies were available, filling in the gaps (if there were any) in the written Homer from the mouths of the rhapsodes. That this collection was more or less for private use and convenience it is reasonable to suppose, and that it showed no accuracy of critical discrimination is a necessary supposition in consideration of its early date.

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## Proceedings of the American Academy of Arts and Sciences.

Vol. XLIII. No. 20. — June, 1908.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

POSITIVE RAYS.

By John Trowbridge.



## CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

#### POSITIVE RAYS.

BY JOHN TROWBRIDGE.

Presented May 13, 1908. Received May 18, 1908.

My intention in undertaking this investigation was to endeavor to measure the group velocity of the positive rays by producing a standing wave, or a stratum of maximum collisions in an exhausted tube in the space between the anode and the cathode. In the case of an oscillating circuit, if we call  $\lambda$  the wave length, v the velocity of light, t the time of a half oscillation, s the distance between the anode and the cathode, v' the velocity of the positive rays, we have

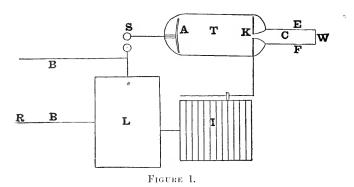
Eq. 1, 
$$\lambda = vt$$
 Eq. 2, 
$$s = v't$$
 
$$t = \frac{\lambda}{r} \qquad v' = \frac{rs}{\lambda}$$

If, by tuning a circuit containing a condenser, self-induction, and the exhausted tube, the strata of maximum collisions could be formed at the orifice in the cathode, it was thought that none of the positive rays would enter the canal region; if, on the other hand, the positive rays swung, so to speak, with the oscillations of the circuit, a maximum fluorescence could be obtained on a suitably placed willemite screen.

The circuit was arranged as follows: A Leyden jar, L, Figure 1, was charged by a storage battery of ten thousand cells, through a large resistance of running water, B. The discharging circuit included an adjustable self-induction, I, a tube filled with rarefied hydrogen, T, and a spark, S. K was an iron electrode, with an orifice two millimeters in diameter at its centre. A glass tube welded to the sides of the tube C entered this orifice. The end of the tube C was coated with willemite.

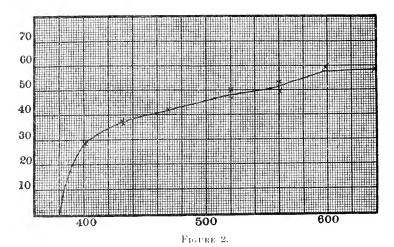
vol. хын. — 33

At first I studied the effect of increasing the self-induction on the admittance of the mixture of anode and cathode rays to the region C.



The phosphorescence on the screen at the end of the tube was observed with a spectrophotometer, and also with a photometer consisting of crossed nichol prisms.

In Figure 2 the intensity of light is plotted along the axis of Y, and the wave lengths of the circuit along X. The phosphorescence



appeared suddenly at wave length 380 meters, and increased to a maximum at wave length 620. The curve then continued parallel to the axis of X. In determining the wave lengths I employed the ad-

mirable wave metre of Professor G. W. Pierce.<sup>1</sup> This instrument enabled me to make measurements in a few moments which otherwise would have required days of labor.

On placing the tube C between the poles of an electromagnet, which produced a field just sufficient to divert the cathode rays from the screen, I found that the changes in the phosphorescence represented in Figure 2 were produced by the cathode rays, for the phosphorescence due to the positive rays remained constant through the range measured. The positive rays were deflected in the direction opposite to that in



FIGURE 3.

which the cathode rays were thrown, by a field of 530 lines to the centimeter, and produced a narrow band on the willemite screen, which showed a slight discontinuity (Figure 3), although the pressure

did not exceed  $\frac{1}{30}$  mm. I was surprised to find that the group of positive rays was so readily deflected by a comparatively weak magnetic field. The length of the band of phosphorescence was 1.5 cm. It is to be noted that the band occurred only on one side of the middle point of the phosphorescent screen.

On discovering that changes in self-induction had no effect upon the intensity of the phosphorescence produced by this group of positive rays, I resolved to damp out all oscillations by introducing a large water resistance in the oscillating circuit. While the dimensions of the discharge tube between the anode and the cathode remained the same as in the experiments described above, the canal region was changed from a circular tube of 3 cm. diameter to the form shown in Figure 4 in plan P and end section E. The width of the cross-section was 3.5 cm. It will be noticed that it had a flattened egg-shaped section, to enable me to place it between the poles of an elec-



P

FIGURE 4.

tromagnet. When all oscillations were damped, and a magnetic field of 500 lines to the centimeter was excited, the positive rays produced

<sup>&</sup>lt;sup>1</sup> Contributions from the Jefferson Physical Laboratory, 4 (1907).

a narrow, sharply defined band of fluorescence, which is represented in the photograph, Figure 5. The middle of the end of the tube is indicated by the sharp pointers on the photograph, and it will be seen that the phosphorescent band extends to approximately equal distances on both sides of the middle of the screen. At first I thought that I was dealing with a mixture of positive and negative rays, and various theories of molecular attraction occurred to me; but experiment showed that all negative rays had been driven out of the field. Moreover, by producing a difference of electrostatic potential, the entire phosphorescent band, or magnetic spectrum, moved in the direction the positive

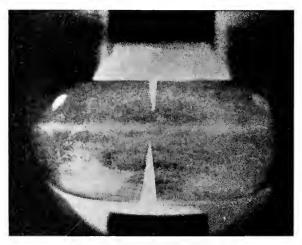


FIGURE 5.

rays should move. In Figure 5 it will be noticed that the band moved to the smaller pointer; whereas, if the portion of the band to the right of the pointers was made up of negative rays, and that to the left of positive rays, the band would not have moved parallel to its original position.

In order to ascertain why the band spread to the right and left of the middle of the screen I introduced a septum of glass in the middle of the tube constituting the canal region (Figure 6). This septum was welded to the end of the tube and was coated on both sides with willemite. The band of phosphorescence now appeared mainly on one side of the partition. By greatly weakening the magnetic field the negative rays were brought upon the screen to the left of the partition, while the positive rays appeared on the right of this partition, thus proving again that the band (Figure 5) was made up of positive rays. A large storage battery proved the best means of studying

the positive band, for the phenomenon was not confused by the make and break of mechanical or electrolytic interrupters. It was soon discovered that a narrow phosphorescent band was formed on the side of the septum which shielded the end of the tube. The explanation of the band in the tube without the septum was evidently this: the pilot spark produces a number of positive rays of different velocities which spread out in the form of a cone, of which the apex is the narrow orifice in the cathode terminal. Under the influence of the magnetic field these rays whirl around in the field somewhat

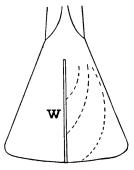


FIGURE 6.

in the manner indicated by the dotted lines (Figure 6).

In the expression  $\rho = \frac{ev'}{mH\sin i}$ ,  $\rho$  can have many values, depending upon the values of v'. The narrowness of the band results from the electrodynamic attraction of the whirls in a manner similar to the attraction of electrical currents all moving in the same direction. The band may be called a magnetic spectrum, since it is produced by many rays of different velocities.

W. Wien 2 has shown that positive rays emanate from the anode, and that these rays can be diverted by an ordinary horseshoe magnet. The rays which I have investigated are undoubtedly of the same nature as those studied by Wien. Their connection, however, with the pilot discharge from a condenser is an added point of interest.

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

<sup>&</sup>lt;sup>2</sup> Wien, Ann., **65**, 449-450 (1898).



## Proceedings of the American Academy of Arts and Sciences.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

CONCERNING THE USE OF ELECTRICAL HEATING IN FRACTIONAL DISTILLATION.

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

Investigations on Light and Heatmade and published, wholly or in part, with Appropriation from the Rumford Fund.



## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

# CONCERNING THE USE OF ELECTRICAL HEATING IN FRACTIONAL DISTILLATION.

BY THEODORE WILLIAM RICHARDS AND JOSEPH HOWARD MATHEWS.

Received May 18, 1908.

In the course of a research 1 now in progress in this laboratory it became necessary to fractionate a number of organic liquids in order to prepare them in a state sufficiently pure for investigation. The process of distillation was at first carried out in the usual manner, but some of the substances required very many successive systematic distillations in order to furnish enough material boiling within a reasonable limit of temperature, and, indeed, in more than one case the task seemed hopeless.

A part of the research in question involved the determination of the latent heat of vaporization of the various substances by means of a modification of Kahlenberg's method,<sup>2</sup> to be described later. In the course of these experiments it was noticed that each organic liquid boiled at a much more constant temperature when heated electrically by the platinum coil of this apparatus than it had during its previous fractional distillations in an ordinary boiling flask. This led to the use of the hot platinum coil instead of the gas burner as a source of heat in the preliminary fractional distillation, with a very great gain in the efficiency of this process.

Probably the reason for this difference in efficiency between the two methods lies in the difference in the extent of superheating. The success of fractional distillation might be supposed to be impaired when superheating occurs, for in this case the higher boiling fractions would naturally have more tendency to come over with those of lower boiling point. In order that the most effective separation may be made, the

<sup>&</sup>lt;sup>1</sup> J. Am. Chem. Soc., **30**, 8 (1908); also Z. phys. Chem., **61**, 449 (1908).

<sup>&</sup>lt;sup>2</sup> Kahlenberg, Journ. Phys. Chem., **5**, 215 (1895).

temperature of the liquid should never exceed the true boiling point of the mixture.

Very considerable superheating occurs when a liquid is boiled in a glass flask by the application of heat from outside. On the other hand, we found that very little superheating of a liquid occurs when the liquid is heated by means of an electric current passing through a suitable resistance wholly immersed in the liquid. S. Lawrence Bigelow has suggested this method of heating in the determination of the molecular weights of a substance in solution by measuring the elevation in boiling points; its satisfactory application to this problem is an indication of its efficiency in obviating superheating. It is clear, therefore, that the electrical method of heating might be expected to give more complete separation during the process of practical distillation than the ordinary method.

The matter is so obvious that probably others have thought of this before; but because we have never seen the method in use, nor have been able to find a reference to it in chemical literature, we venture to call attention to it in this brief paper.

The extent of the increased efficiency is best indicated by two parallel experiments, alike in every essential respect except the difference in the source of heat, and the fact that into the ordinary boiling flask Markovnikov capillary tubes were placed to relieve the superheating to some extent. Even with this precaution added to the old way, the difference in result was very marked, as the following figures show.

0.1 liter of a specimen of normal butyl alcohol, dried with anhydrous copper sulphate, needed six distillations in order to secure 75 milliliters of liquid boiling within the limits of 1 degree (117.0°-118.0° at 759 mm.), using the ordinary method of outside heating by a gas flame.

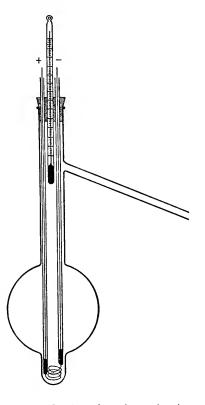
The same volume of the original liquid by only *two* fractional distillations with electrical heat yielded the same volume of distillate of a much higher grade of purity, having boiling-point limits only 0.6 apart (117.3°-117.9°).

Similarly, 120 milliliters of ortho cresol which in one distillation gave 100 milliliters within 0.8° (190.0°-190.8° at 765.0 mm.) gave an equal amount boiling within 0.3° (189.9°-190.2° at 758.5 mm.) by the new method. Numerons other examples might be cited, but these are sufficient to show the great advantage to be derived from electrical heating.

A word concerning an advantageous form of apparatus is not out of place, although a heating resistance-coil may be immersed under the liquid in any ordinary distilling apparatus. In order to economize

material, a narrow cistern was blown into the bottom of a common stout distilling flask. Into this depression the heating coil was placed. The coil consisted of about 40 centimeters of platinum wire having a

resistance of about 0.7 ohms. current of from ten to fifteen amperes was led to the resistance wire from above by heavy copper wires encased in glass tubes, into the ends of which the ends of the platinum wire were sealed, contact being made by a drop of mercury. It is necessary that these copper wires be heavy (about 2.5-3.0 mm. in diameter), so that they may not become heated by the current and thus superheat the vapor coming into contact with the glass tubes encasing them. For this reason it might be well to introduce the electrical connection from below, through the glass walls of the cistern; but obviously the present arrangement can be most easily made. It is necessary that the coil and mercury contacts be entirely covered by the liquid at all times. The diagram illustrates the arrangement. The coil was more compact than that represented in the figure, so that it was possible to distil all but four or five milliliters without uncovering the resistance.



It is almost needless to call attention to the fact that short-circuiting through the liquid may cause slight decomposition when electrolytes are thus heated; hence the method is not well applicable to liquids of this class.

Because the bubbles of vapor arise only from the small area of the hot resistance wire, ebullition proceeds quietly, and there is never any tendency to "bump." This method of heating is therefore especially applicable to fractional distillations under reduced pressure, where so much trouble is usually experienced from the explosive formation of vapor. Concentrated sulphuric acid, for example, boils as quietly under greatly reduced pressure when so heated as does water or

alcohol under ordinary pressures. The method of heating dispenses entirely with the necessity of passing air through the liquid in vacuum distillations, and heavy viscous liquids may be advantageously distilled in this way. By combining this method of heating with the Hempel, Wurtz, Linnemann, or other fractionating towers, great efficiency may be expected. However, where the amount of material is small, the towers cannot be advantageously used, because of the loss of material required to wet the considerable area of their condensing surfaces; and it is very convenient to have at hand an economical method fully as efficient as the ordinary method where the tower is used.

The method may also find successful application in the distillation of inflammable liquids, and may therefore be of some industrial importance where power may be obtained cheaply. Moreover, low boiling liquids, ordinarily requiring special precautions, can be distilled as expeditiously as those of high boiling point, since superheating is impossible.

In brief, this article describes experiments showing the great gain in the efficiency of separation obtainable by the use of electricity as a source of heat in fractional distillation. An advantageous form of apparatus for this purpose is described.

THE CHEMICAL LABORATORY OF HARVARD COLLEGE.





## Proceedings of the American Academy of Arts and Sciences.

Vol. XLIII. No. 22. - July, 1908.

RECORDS OF MEETINGS, 1907-1908.

REPORT OF THE COUNCIL: BIOGRAPHICAL NOTICE.

SAMUEL CABOT. BY CHARLES LORING JACKSON.

OFFICERS AND COMMITTEES FOR 1908-1909.

LIST OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

STATUTES AND STANDING VOTES.

RUMFORD PREMIUM.

INDEX.

(TITLE PAGE AND TABLE OF CONTENTS).

## RECORDS OF MEETINGS.

Nine hundred seventy-fifth Meeting.

OCTOBER 9, 1907. — STATED MEETING.

The President in the chair.

There were present twenty-four Fellows.

The Corresponding Secretary, pro tempore, read letters from G. W. Pierce, accepting Fellowship; from the California Academy of Sciences, thanking the Academy for the contribution of its publications; from Arthur McDonald, asking the Academy to form resolutions regarding the establishment of laboratories for the study of the criminal, pauper, and defective classes, and transmitting a pamphlet on the subject; from C. van Overbergh, Directeur général de l'Administration de l'Ensignment Supérieur des Sciences et des Lettres, enclosing a copy of the report of the International Congress for the Study of the Polar Regions, and requesting the publications of the Academy; from St. C. Hepites and I. St. Murat, notifying the Academy of their appointment as Directors of the Roumanian Meteorological Institute and Service Central des Poids et Mesures; from Vilh. Thomsen, President of the International Congress of Orientalists, inviting the Academy to send delegates to the Fifteenth Congress, in August, 1908; from President Capellini, two communications relative to the celebration of the anniversary of the death of Aldrovandi; from the Société Géologique de Belgique, notifying the Academy of the death of its Secretary, Henri-Joseph Fourir; from the Astrophysical Observatory, Potsdam, notifying the Academy of the death of H. C. Vogel; from the Kön, böhmische Gesellschaft der Wissenschaften, notifying the Academy of the death of Johann Gebauer, and also of the death of J. Bohuslav, Freih. v. Rieger.

The Chair announced the following deaths: -

Charles F. Folsom, Resident Fellow, of Class II, Section 4; H. C. Vogel, Foreign Honorary Member of Class I, Section 1; and of Henry G. Denny, a former Resident Fellow.

On the recommendation of Professor Webster, it was

Voted, That an unexpended balance of \$93.46 from the income of the Rumford Fund, returned by Professor Edwin H. Hall, be reappropriated to the use of the Rumford Committee.

The following gentlemen were elected Resident Fellows of

the Academy: -

James Flack Norris, of Boston, in Class I, Section 3 (Chemistry).

William Hultz Walker, of Newton, in Class I, Section 3

(Chemistry).

Mr. A. T. Thompson showed the use of his reflectoscope in projecting photographs and opaque objects upon the screen.

On motion of the Recording Secretary, it was

Voted, That the thanks of the Academy be tendered to Mr. Thompson for his interesting exhibition of the reflectoscope.

Dr. Theodore Lyman gave a paper entitled "The Absorption of the Air for Light of very Short Wave Lengths."

The following paper was presented by title: -

"Difference in Wave Lengths of Titanium λλ 3900 and 3913 in Arc and Spark." By Norton A. Kent and Alfred H. Avery. Presented by John Trowbridge.

#### Nine hundred seventy-sixth Meeting.

## NOVEMBER 13, 1907.

VICE-PRESIDENT WALCOTT in the chair.

There were present twenty-seven Fellows.

The following letters were read:—

From Wm. H. Walker, accepting Fellowship; from Dr. G. Hellman, announcing his appointment as Director of the Kön. Preuss. Meteorologisches Institute of Berlin; from the Verein für Naturwissenschaft in Braunschweig, announcing the death of Professor Dr. Rudolf Blasius.

The Chair announced the following deaths: -

Edward G. Gardiner, Resident Fellow in Class II, Section 3.

Sir Benjamin Baker, Foreign Honorary Member in Class I, Section 4.

The following communications were given: -

"The Volcanoes of the Azores." By Professor W. H. Pickering.

"The Linnaean Celebration at Upsala, Sweden." By Professor W. G. Farlow.

The following paper was read by title: -

"A Revision of the Atomic Weight of Lead. Preliminary Paper: The Analysis of Lead Chloride." By Gregory Paul Baxter and John Hunt Wilson.

#### Nine hundred seventy-seventh Meeting.

## DECEMBER 11, 1907.

The President in the Chair.

There were present seventeen Fellows.

Letters were read from Arthur I. Davenport, announcing the death of his father, George E. Davenport; from the Sixteenth International Congress of Americanists, inviting the Academy to send delegates.

The Chair announced the death of George E. Davenport, Resident Fellow in Class II, Section 2, and also of Professor Minton Warren, whose nomination had been read to the Academy at its last meeting.

On motion of Professor Davis, it was

Voted, That in reference to the death of Professor Warren the President be authorized to take such action as he thinks proper.

On motion of Professor Davis, it was

Voted, That the House Committee be authorized to provide a simple collation for the Members at the meetings of the Academy.

The following communications were given: -

"The Most Recent Exploration in Palestine." By Professor D. G. Lvon.

"The Centenary Celebration of the Geological Society of London," By Professor W. M. Davis,

The following papers were presented by title: -

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"The Influence of Hysteresis upon the Manner of Establishment of a Steady Current in the Primary Circuit of an Induction Coil." By B. O. Peirce.

"Some Effects of Heavy Pressure on Arc Spectra." By W.

J. Humphreys. Presented by C. R. Cross.

"The Effect of a Magnetic Field on the Cathode Rays." By John Trowbridge.

#### Nine hundred seventy-eighth Meeting.

JANUARY 8, 1908.—STATED MEETING.

The President in the chair.

There were present twenty Fellows.

Letters were read from the Secretaries of the Third International Congress for the History of Religions, enclosing the first announcement of the Meeting to take place at Oxford in September, 1908, and inviting the Academy to send a Representative; from the Physikalische Verein of Frankfort, informing the Academy of the opening of the new Institute Building, and inviting the Academy to send Delegates; from the Committee of Organization, informing the Academy of the First Congress of Chemistry and Physics to be held at St. Petersburg in January, in memory of D. I. Mendéléeff.

The following deaths were announced by the Chair: —

Lord Kelvin, Foreign Honorary Member in Class I, Section 4; Charles A. Young, Associate Fellow in Class I, Section 1; Thomas D. Seymour, Associate Fellow in Class III, Section 2.

The following Delegates were appointed to represent the Academy at the Fifteenth International Congress of Orientalists, to be held at Copenhagen in August, 1908:—

Charles R. Lanman, George F. Moore.

In answer to an inquiry by Professor Webster, on motion of Colonel Livermore, it was

Voted, That the Corresponding Secretary be requested to ascertain and report to the Academy on the measures to be taken in reference to the Nobel Prizes.

Le Baron Russell Briggs was elected a Resident Fellow in Class III, Section 4 (Literature and the Fine Arts).

The following communications were presented:—

"Cretan Chronology." By President W. W. Goodwin.

"The Polariscope and the Weather." By Dr. Louis Bell.

The following paper was read by title:

"A Simple Method of Measuring the Intensity of Sound." By George W. Pierce.

#### Nine hundred seventy-ninth Meeting.

## February 12, 1908.

The Corresponding Secretary pro tempore in the chair. There were present twenty-four Fellows.

Letters were read from the Sub-director of the Museo Nacional, Mexico, felicitating the Academy on the New Year: from the Committee of the Fourth International Congress of Mathematicians to be held at Rome, April 6-11, 1908.

The death of Edward H. Strobel, Resident Fellow in Class III, Section 1, was announced.

The following report of the House Committee was read and accepted:—

"At the meeting of the Academy held on the eleventh of December, the House Committee were instructed to consider and report whether it would be advisable for the Academy to provide a light repast, consisting of crackers, ale, and cheese, at the conclusion of the meetings.

"We find that the expense involved would be about twenty-five dollars for tables and dishes, and an annual outlay of about twenty-five dollars. After consulting the Treasurer, we recommend that these sums be expended, the initial outlay being paid by the appropriation for House expenses, and the current expense charged to the appropriation for the expense of meetings.

"The Committee have, as has been announced, provided a ventilator in the meeting-room, with an air-shaft reaching above the roof, which it is hoped will prove effective. If not, it can be made more so by putting an electric fan into the air-shaft.

"Meanwhile it has been urged upon them that the present meetingroom shall be given up, and a larger and pleasanter one be constructed in the front of the house in the third story. A room could be made covering about six hundred and fifteen square feet, about a third more than the area of the present room, which covers four hundred and sixty-five square feet. The cost would be about thirteen hundred dollars (\$1300), a larger sum, considerably, than the means at the Treasurer's command can supply. But if the ventilation now proposed proves on trial unsatisfactory, and it is found that the cost of these changes can be raised, as has been suggested, by subscription, and, at the close of the season, the Academy so vote, the alteration can be made in the course of the summer."

On motion of Professor Webster, and seconded by Professor Kinnieutt, it was

Voted, That the House Committee be requested to consider the question of raising funds for the carrying out of the plans for a meeting-room on the third floor.

Professor George F. Moore was appointed a Delegate to the Third International Congress for the History of Religions, to be held at Oxford in September, 1908.

Professor Jaggar informed the Academy that there was a bill pending in the Legislature for a new topographical survey of the State.

Professor T. A. Jaggar gave the following communication: -

"Volcanoes of the Aleutian Islands."

The following papers were read by title: -

"Measurements of the Internal Temperature Gradient in Common Materials." By Charles B. Thwing. Presented by C. R. Cross.

"The Variation of the Thermomagnetic Effect in Soft Iron with Strength of the Magnetic Field and Temperature Gradient." By L. L. Campbell. Presented by John Trowbridge.

#### Nine hundred eightieth Meeting.

MARCH 11, 1908. — STATED MEETING.

VICE-PRESIDENT TROWBRIDGE in the chair.

There were present twelve Fellows.

Letters were read from L. B. R. Briggs, accepting Fellowship; from William W. Goodwin, declining re-election as President of the Academy; from the Geological Society of London, thanking the Academy for delegating Professor W. M. Davis

to attend its centenary, and presenting to the Academy the volume, "The History of the Geological Society of London"; from the Académie des Sciences, Agriculture, Arts et Belles-Lettres, of Aix, requesting delegates from the Academy to attend the celebration of the centenary of its Reconstitution; from the Gesellschaft von Freunden der Naturwissenschaften, notifying the Academy of its fiftieth anniversary.

The Chair announced the following deaths: —

Asaph Hall, Class I, Section 1; Israel C. Russell, Class II, Section 1; Augustus St. Gaudens, Class III, Section 4; E. C. Stedman, Class III, Section 4, Associate Fellows.

The Chair appointed for Nominating Committee: -

Charles R. Cross, of Class I.

Charles S. Minot, of Class II.

Morris H. Morgan, of Class III.

It was

Voted, To meet on adjournment on the second Wednesday in April.

Dr. G. H. Parker presented the communication:

"The Influence of Light on the Daily Activities of Animals." The following papers were read by title:—

- "The Damping of the Quick Oscillations of a Twisted Fibre by the Resistance of the Air and by the Torsional Forces." By B. O. Peirce.
- "Notes on Superheated Steam: I, Its Specific Heat; II, Its Total Heat; III, Its Joule-Thomson Effect." By Harvey N. Davis. Presented by W. C. Sabine.
  - "The Sensory Reactions of Amphioxus." By G. H. Parker.
- "On Delays before ἀναγνωρίσεις in Greek Tragedy." By W. P. Dickey. Presented by M. H. Morgan.

#### Nine hundred eighty-first Meeting.

APRIL 8, 1908. — ADJOURNED STATED MEETING.

The Academy met by invitation of Professor Elihu Thomson at the Algonquin Club, 217 Commonwealth Avenue.

VICE-PRESIDENT TROWBRIDGE in the chair.

There were present forty-nine Fellows and four guests.

The following gentlemen were elected members of the Academy: —

Louis Derr, of Brookline, as Resident Fellow in Class I, Section 2 (Physics).

John Ulric Nef, of Chicago, as Associate Fellow in Class I, Section 3 (Chemistry).

On the recommendations of the Recording Secretary, the Chairman of the Rumford Committee, and the Chairman of the Publishing Committee, it was

Voted. To make the following appropriations: From the income of the General Fund, for House expenses, \$425; for Books and binding, \$340; for Meeting expenses, \$35; from the income of the Rumford Fund, for the furtherance of research, \$141.90 (the unexpended balance of a previous grant); from the income of the Publication Fund for publication, \$800.

Vice-President Trowbridge announced that the Rumford Premium had been awarded to Mr. Edward Goodrich Acheson for the application of heat in the electric furnace to the industrial production of carborundum, graphite, and other new and nseful substances. He then called upon the chairman of the Rumford Committee, Professor Charles R. Cross, who gave a short account of the previous awards of the Rumford Medal, followed by a brief analysis of Mr. Acheson's work and the circumstances which influenced the Committee to recommend the award to him.

Vice-President Trowbridge then presented the medal in the name of the Academy to Mr. Acheson, who expressed his appreciation of the honor conferred upon him, saying: "The medal has been a great incentive to me from boyhood, and I had hoped sometime to attain it. To-night my dream has come true."

On the invitation of the Chair he then gave an account in detail of his discoveries, illustrated by a number of interesting demonstrations.

The following papers were presented by title:—

"The Invariants of Linear Differential Expressions." By Frank Irwin. Presented by Maxime Bôcher.

"Contributions toward a Monograph of the Laboulbeniaceae. Part II." By Roland Thaxter.

#### Nine hundred eighty-second Meeting.

## MAY 13, 1908. — ANNUAL MEETING.

VICE-PRESIDENT WALCOTT in the chair.

There were present twenty-eight Fellows.

Letters were read from Thomas Dwight, Theodore Hough, and Arthur Michael, resigning Fellowship; from Louis Derr, accepting Fellowship; from the Third International Congress of Botany, two circulars referring to the Congress.

The death of Gustavus Hay, Resident Fellow in Class I, Section 1, was announced by the Chair.

The annual report of the Council was read.1

The annual report of the Treasurer was read, of which the following is an abstract:—

#### GENERAL FUND.

| •                                                                    |    |      |      |      | $I_{\ell}$  | lece | ipt  | 8.   |    |                            |                                           |
|----------------------------------------------------------------------|----|------|------|------|-------------|------|------|------|----|----------------------------|-------------------------------------------|
| Investments . Assessments . Admission fees Rent of offices           |    | <br> |      |      |             |      |      |      |    | $1,830.00 \\ 70.00$        | \$5,933.41                                |
|                                                                      |    |      |      | E    | a pe        | end  | itu. | res. |    |                            |                                           |
| General expenses<br>Library<br>Income transferr<br>Balance, April 36 | ed | to p | rino | cipa | l           |      |      |      |    | $1,759.67 \\ 758.49$       | \$5,552.41<br><u>381.00</u><br>\$5,933.41 |
|                                                                      |    |      |      | Rτ   | MF          | ORI  | F    | UN   | D. |                            |                                           |
|                                                                      |    |      |      |      | $R\epsilon$ | cei, | pts. |      |    |                            |                                           |
| Balance, April 36<br>Investments                                     |    |      |      |      |             |      |      |      |    | $\frac{$186.86}{3,027.90}$ | \$3,214.76                                |

<sup>&</sup>lt;sup>1</sup> See p. 547.

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| Larper | ditures. |

|                                                               |                | " Pon  |                                       | U.•         |                                                |                                           |
|---------------------------------------------------------------|----------------|--------|---------------------------------------|-------------|------------------------------------------------|-------------------------------------------|
| Research                                                      | incipa         | <br>   | · · · · · · · · · · · · · · · · · · · | •           | 341.50                                         | \$2,463.58<br><u>751.18</u><br>\$3,214.76 |
|                                                               | C. M.          | WAI    | RREN                                  | Fuxi        | D <b>.</b>                                     |                                           |
|                                                               |                | Rece   | ipts.                                 |             |                                                |                                           |
| Balance, April 30, 1907<br>Investments                        |                |        |                                       |             |                                                | \$1,463.30                                |
|                                                               | E              | Tapeno | liture:                               | 3.          |                                                |                                           |
| Research                                                      | ed off         | <br>   |                                       | ·<br>·<br>· | . \$ 150.00<br>. 4.00<br>. 90.00<br>241.37<br> | \$ 485.37<br>977.93<br>\$1,463.30         |
|                                                               | Риві           | LICATI | on F                                  | UND.        |                                                |                                           |
|                                                               |                | Rece   | ipts.                                 |             |                                                |                                           |
| Balance, April 30, 1907<br>Investments Sale of publications . |                |        |                                       |             | . 3,179.02                                     | \$3,540.06                                |
|                                                               | $E_{\epsilon}$ | vpend  | itures                                |             |                                                |                                           |
| Publication                                                   | incipa         | · .    |                                       |             |                                                | \$3,195.76<br>344.30<br>\$3,540.06        |

## The following reports were also presented: —

## REPORT OF THE LIBRARIAN.

Of the library catalogue there remains to be done the serial publications on general science, comprising the two lower floors of the stack building, and the few books on literature, the fine arts, and religion. The Academy is fortunate in having this work done by so accomplished a cataloguer as Miss Wyman, and at such a moderate cost, the last advantage resulting from the fact that Miss Wyman gives only a portion of her time to the Academy.

The Assistant Librarian is endeavoring to complete the sets of Society publications now in the library by sending to the various societies a request for each missing number, and offering in return to complete their sets of the Academy's publications. In a great many cases the request is complied with, in others the numbers requested are scarce or out of print. These could perhaps be purchased of second-hand booksellers were money available for the purpose. This lack of money is much to be regretted, as in time it will be practically impossible to purchase them.

The accessions during the year have been as follows: -

|                            | Vols. | Parts of Vols. | Pams.           | Maps. | Total. |
|----------------------------|-------|----------------|-----------------|-------|--------|
| By gift and exchange       | 234   | 2076           | 76              | 5     | 2391   |
| By purchase — General Fund | 12    | 538            |                 |       | 550    |
| By purchase — Rumford Fund | 5     | 327            |                 |       | 332    |
| Total                      | 251   | 2941           | $\overline{76}$ | 5     | 3273   |

The bound volumes in the library have been counted since the last report, and there are now 29,089 volumes. Hereafter in this report the accessions will be given in volumes, and not by parts, as heretofore, and will represent the volumes placed on the shelves during the preceding year.

80 books have been borrowed from the library by 24 persons, including 13 Fellows, and two libraries (Clark University and the University of Cincinnati).

All books borrowed during the year have been returned for the annual examination. Of the books reported as still out a year ago, all have been returned.

The expenses charged to the library are as follows: Miscellaneous, \$519.67 (which includes \$175.93 for cataloguing); Binding, \$585.55 General, and \$56.35 Rumford, Funds: Subscriptions, \$654.45 General, and \$142.75 Rumford, Funds; making a total of \$1240.00 for the

General, and \$199.10 for the Rumford, Funds, as the cost of subscriptions and binding. Of the appropriation of \$50.00 from the Rumford Fund for books, five have been purchased at a cost of \$23.64.

Although \$585.55 from the income of the General Fund was spent for binding, there are still 400 volumes waiting to be bound. There has never been an adequate amount appropriated for binding, and we are now exchanging with more societies and universities than ever before. Societies are now publishing more volumes, and these contain more plates than formerly, which makes the binding more expensive.

A. LAWRENCE ROTCH, Librarian.

May 13, 1908.

## REPORT OF THE RUMFORD COMMITTEE.

From the amount available for the purpose, the Committee during the year 1907-08 has made grants as follows, for the furtherance of researches in light and heat:—

researches in light and heat: — June 12, 1907. P. W. Bridgman, of the Jefferson Physical Laboratory, for the continuation of his work on the optical and thermal properties of bodies under extreme pressure . . . . \$400 Oct. 9, 1907. P. W. Bridgman, in addition to the above appropriation, for the same purpose 400Jan. 8, 1908. Dr. L. J. Henderson, of the Harvard Medical School, in aid of his research on a new method for the direct determination of physiological heats of reaction . . . . 200Feb. 12, 1908. Professor Joel Stebbins, of the University of Illinois, for his research on the use of selenium in photometry. 100 Feb. 12, 1908. Mr. Willard J. Fisher, of Cornell University, for his research on the viscosity of gases . . . . . . . . . Reports stating the progress of their respective investigations have

Reports stating the progress of their respective investigations have been received from Messrs. P. W. Bridgman, A. L. Clark, E. B. Frost, L. J. Henderson, L. R. Ingersoll, N. A. Kent, F. E. Kester, H. W. Morse, E. F. Nichols, A. A. Noyes, J. A. Parkhurst, T. W. Richards, R. W. Wood.

Since the last annual meeting the following papers have been published at the expense of the Rumford Fund, the first-mentioned in the Memoirs, the others in the Proceedings:—

"High Electromotive Force." John Trowbridge, May, 1907.

"Studies on Fluorite: IV, The Kathodo-Luminescence of Fluorite." H. W. Morse. June, 1907.

"The Physiological Basis of Illumination." L. Bell. September, 1907.

"The Transition Temperature of Manganous Chloride: A New Fixed Point in Thermometry." T. W. Richards and F. Wrede. November, 1907.

"Difference in Wave-Lengths of Titanium λλ 3900 and 3913 in Arc and Spark." N. A. Kent and A. H. Avery. November, 1907.

"Note on Some Meteorological Uses of the Polariscope." L. Bell. March, 1908.

At its meeting of Jan. 8, 1908, the Committee, at the request of the Librarian, voted an appropriation of \$50 for the binding of books and periodicals relating to light and heat.

The Committee is endeavoring to make a complete list of all apparatus purchased in past years through appropriations from the Rumford Fund, and hence at present the property of the Academy, to the end that such apparatus, if suitable, may be available for purposes of research in the future.

Charles R. Cross, Chairman.

May 13, 1908.

#### REPORT OF THE C. M. WARREN COMMITTEE.

The C. M. Warren Committee beg leave to report that grants have been made during the past year to the following persons, in aid of the researches specified:—

Dr. Frederic Bonnet, Jr., Worcester Polytechnic Institute . S150 "The Effect of Lanthanum, Cerium, and Neodymium Oxides upon Porcelain Glazes, especially as regards their Electrical Conductivity."

"A Study of the Structure of Triphenyl Methyl."

The work of Professor J. Bishop Tingle on the "Study of the Action of Certain Secondary Amines on Camphoroxalic Acid," to aid which research a grant of \$50 was made by the Warren Committee in 1907, has been published in the American Chemical Journal, and acknowledgment made in the paper for the grant received from the Warren Committee.

A report of the progress made has also been received from Dr. Frederic Bonnet, Jr., and the result of his investigations will, it is hoped, be published the coming year.

LEONARD P. KINNICUTT, Chairman.

May 13, 1908.

#### REPORT OF THE PUBLICATION COMMITTEE.

Between May 1, 1907, and May 1, 1908, there were published of the Proceedings, three numbers of Volume XLII (Nos. 27–29), and sixteen numbers of Volume XLIII; also one biographical notice, — in all 567 + v pages and four plates. Five numbers of Volume XLIII (Nos. 1, 4, 10, 11, and 15) were paid for from the income of the Rumford Fund.

There has also been published, at the expense of the Rumford Fund, one Memoir (Volume XIII, No. 5, pp. 188-215, plates xxv-xxvii).

There are in press two numbers of the Proceedings; and an extensive Memoir of some three hundred pages, illustrated with forty-four plates, is in type. This will complete Volume XIII of the Memoirs.

The Academy placed at the disposal of the Publication Committee, from the income of the Publication Fund, \$3200. Of this amount, \$3046.55 have been paid by the Treasurer on bills approved by the chairman of the Committee, leaving a balance of \$153.45.

Bills aggregating \$473.51 incurred in publishing Rumford papers have been forwarded to the chairman of the Rumford Committee for approval.

## REPORT OF HOUSE COMMITTEE.

During the last year the lower story of the Academy's House has been occupied by the three physicians to whom it has been leased; the second story by the Academy itself, the Meeting Room being in the rear, and the Reception Room and the Librarian's Office being in the front; the third story by the dwelling rooms of the Assistant Librarian, and the fourth story by storerooms and workroom, and a bedroom for the Janitor. Under this arrangement the building has been almost constantly occupied in one part or another, and its contents have been properly guarded.

The bills approved by the Secretary of the Academy and the Chairman of this Committee, and paid by the Treasurer, have amounted to \$1624.62, of which \$1200 was especially appropriated at the beginning of the year, and the balance, amounting to \$414.62, was made up from unappropriated funds in the hands of the Treasurer by a subsequent vote of the Academy. These amounts include \$11.50 spent for the tables and dishes used for the slight repasts which have been furnished to the members at the close of the meetings. The sum of \$16.02, which has been the total cost of five such entertainments, coming to about \$3.30 apiece, has been charged to the expense of the meetings.

The Committee have spent \$163.77 in improving the ventilation of the Meeting Room, an amount included in the previous statement.

The ventilation will probably be still further improved by the change recently made in the seating, which will enable the southern windows to be opened. This will, we expect, make the ventilation entirely satisfactory.

But some objection has also been made to the general aspects of the Meeting Room and its somewhat contracted appearance. The Academy accordingly at the February meeting directed this Committee to consider and report upon the practicability of building a somewhat larger Meeting Room in the front of the third story, over the present Reception Room. We find that this could be done at a cost of between \$1200 and \$1500, the new room promising to be about one-third larger than the present one.

But as the Academy has not this amount of money in hand, and, as the leases of the first floor will expire within a reasonable time, we think that it would be better for the Academy to try meanwhile to raise money enough to enable it to dispense with the leasing of the first floor and to fit up a commodious meeting room there, and we recommend that steps be taken towards this end.

WILLIAM R. WARE, Chairman.

May 13, 1908.

## FINANCIAL REPORT OF THE COUNCIL.

| as follows                                                                                                                 | the year 1908-09, as estimated by the Treasurer, is $ \begin{cases} \text{Investments} & . & . & . & . & . & . & . & . & . & $                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |  |  |  |
|----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|
| Publication Fund                                                                                                           | Appleton Fund investments \$ 559.52<br>Centennial Fund investments 2236.75 \$2796.27                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |  |  |  |
| RUMFORD FUND                                                                                                               | Investments                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |
| WARREN FUND                                                                                                                | Investments                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |
| The above estimates, less 5 per cent to be added to the capital, leaves an income available for appropriation as follows:— |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |  |  |  |
| General Fund .                                                                                                             | \$4262.62         2656.46         2563.14                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |  |  |  |
| Publication Fund                                                                                                           | $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ |  |  |  |  |
| Rumford Fund .                                                                                                             | $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ |  |  |  |  |
| Warren Fund                                                                                                                | 601.19                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |  |  |  |

# The following appropriations are recommended —

## General Fini

| Library expenses  Books, perphinals, and binding  Extenses of meetings |    |  | \$1200<br>1600<br>270<br>270<br>170 | <u>\$4</u> 1(0)               |
|------------------------------------------------------------------------|----|--|-------------------------------------|-------------------------------|
| Fiblication Fire                                                       |    |  | ,                                   | $\hat{S}_{ij}^{2} \neq [\pi]$ |
| Roman Fon.                                                             |    |  |                                     |                               |
| Research Penphysis and tinding Books and tinding Publication           |    |  | 150                                 |                               |
| To be ased at distretion of Committee  C 21 Warrant Ft                 | Y. |  | <u> </u>                            | <u>\$</u> 2566                |

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In accordance with the recommendations in the foregoing error of Mas

The Trappropriate for the purposes named the following sums. —

| Ξ.: | == == ====                              | iime if the  | General Fund   | \$4100     |
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| Ē.  |                                         |              |                | 2568       |
| F:: |                                         | orale of the | J. M. Watten B | Pari . 500 |

On the motion of the Treasurer, it was

. The i That the assessment for the ensuing year be ten inflars (81).

The annual electron resulted in the choice of the following officers as is summittees:—

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Erms H. Hall. I may also Sent g.

William Watson, Recold = Secretary, Charles P. Bowlitth, T = 10000, A. Lawrence Rotch, Letter to the secretary

Constant Three Years

William L. Hooper, of Class I, Harold C. Ernst, of Class II. Frederic J. Stimson, of Class III.

F one the star

John Thowbridge, Eliot C. Clarke, Francis Baltlett

 $R' = \{i \in C, \dots, \dots \}_{i \in S}$ .

CHARLES R. Causs. ARTHUR G. WEBSTER.

EDWARD C. Pichesing. Eliet Teomson.

ERASMUS D. LEAVITT. THEIDDRE W. RITHARIS.

Litis Bell.

 $C,\ M,\ \overline{M},\ c_2,\quad C,\quad c_3,\quad c_4,\quad$ 

Leinard P. Kinnicutt. Charles R. Sanger.

Robert H. Richaels. Arthur A. Nites. Henry P. Taleot. Theology W. Richaels.

George D. Miniae.

The following standing committees were chosen:—

 $P_{\alpha}^{\text{prin}} = C_{\alpha} = C_{\alpha}^{\text{prin}}$ 

Wallace C. Sarine, of Class I. Edward L. Mare, of Class II. Crawford H. Tov. of Class III.

In June 19

Habey M. Godowin, of Class I. Samtel Henseaw, of Class II. Hensy W. Hafnes, of Class III.

A MODELL THE

A. Lawrence Lowell. Frederic J. Stimson.

E. s. Committee

William R. Ware. A. Lawrence Ritte. Moreis H. Illegan.

On motion of the Recording Secretary, the following Resolution was unanimously adopted:—

Resolved, That the Fellows of the American Academy desire to place upon record their grateful appreciation of the services of their retiring President, William W. Goodwin, during the five years in which he has presided over their deliberations.

The following gentlemen were elected members of the Academy:

Douglas Wilson Johnson, of Cambridge, as Resident Fellow in Class II., Section 1 (Mathematics and Astronomy).

Charles Hyde Warren, of Auburndale, as Resident Fellow in Class II., Section 1.

Emil Fischer, of Berlin, as Foreign Honorary Member in Class I., Section 3 (Chemistry), in place of the late D. Mendeleeff.

Professor A. G. Webster gave a communication entitled: "Absolute Measurements of Sound."

The following papers were presented by title: -

- "A new Method of Determining the Specific Heats of Solutions. By T. W. Richards and A. W. Rowe.
  - "Positive Rays." By John Trowbridge.
- "Variation of the Thermomagnetic Effect in Soft Iron." By L. L. Campbell. Presented by John Trowbridge.
- "The Latent Heat of Fusion and the Specific Heat in the Solid and Liquid State of Salts Melting below 600° C." By H. M. Goodwin and H. T. Kalmus.
- "Pisistratus and his Edition of Homer." By Samuel Hart Newhall. Presented by M. H. Morgan.

# AMERICAN ACADEMY OF ARTS AND SCIENCES.

REPORT OF THE COUNCIL. - PRESENTED MAY 13, 1908.

BIOGRAPHICAL NOTICE.

SAMUEL CABOT . . . . . . . . . . . By Charles Loring Jackson.



# REPORT OF THE COUNCIL.

The Academy has lost fourteen members by death since the last report of the Council, — five Resident Fellows, Charles F. Folsom, Edward G. Gardiner, George E. Davenport, Edward H. Strobel, Gustavus Hay; six Associate Fellows, T. D. Seymour, C. A. Young, Asaph Hall, I. C. Russell, A. St. Gaudens, E. C. Stedman; three Foreign Honorary Members, H. C. Vogel, Sir Benjamin Baker, Lord Kelvin.

Three Resident Fellows have resigned.

Seven Resident Fellows have been elected.

One Resident Fellow has been elected to Associate Fellowship.

The roll of the Academy now includes 187 Resident Fellows, 92 Associate Fellows, and 65 Foreign Honorary Members.

#### SAMUEL CABOT.

Samuel Cabot, the fourth of the name, was born February 18, 1850, in Boston, where his father was an eminent surgeon. His grandfather, a successful East India merchant in the days before commercial supremacy had left New England, married Elizabeth Perkins, the daughter of Thomas Handasyd Perkins, founder of the Perkins Institution for the Blind. His mother, Hannah Lowell Cabot, was the daughter of Patrick Tracy Jackson, of Boston, celebrated for the introduction of the manufacture of cotton goods into America at Waltham and Lowell, and of Lydia Cabot, of Beverly. He was therefore descended on each side from a family noted for rugged independence, sturdy honesty, and devotion to high ideals.

He was the oldest son but second child in a numerous family dominated by the high ideals of which I have just spoken, as his father was one of the most vigorous supporters of the antislavery cause when this could not be done without sacrifice, and in this and all other matters the pursuit of the highest at any cost was impressed on the children by the precept and example of both parents. The life in his earlier days in Boston, and in the summer at Canton, was of necessity simple; those were the days of small fees, when a surgeon, even of his father's eminence, gained an income barely sufficient for the support of

a large family. In fact, it was characteristic of Dr. Cabot that even to the day of his death he remained an uncompromising opponent to the high charges for surgical work which had already appeared. But if the life was simple, it was very full and happy; the family circle was bound together by a warm, almost passionate affection, and was surrounded by troops of friends both in Boston and in the country. All the burning questions of the day were discussed continually with great energy by the brothers and sisters, each one of whom was thoroughly convinced of the truth of his or her opinion and never backward in proclaiming it. The home atmosphere was therefore stimulating, both morally and mentally.

He was educated in the public schools, finally at the Boston Latin School, from which he graduated in 1866. Here he proved himself a painstaking but not brilliant scholar, as, like so many healthy boys, his interests were in athletic sports, especially baseball and football, rather than in his books.

On leaving the Latin School he was naturally attracted by the Massachusetts Institute of Technology, then in its infancy, since he inherited strong scientific tastes from his father, who was an excellent ornithologist and in his younger days had made scientific journeys. It is probable, however, that the impulse to chemistry came from the Jacksons, as his contemporaries in this family included nine professional chemists divided among three branches of the family, which had separated in the seventeenth century. If this does not indicate a strong family taste for chemistry, but is a mere coincidence, it is certainly a strange one, as chemistry is distinctly an unusual profession. Accordingly he entered the Institute in the third class received by it, and devoted his attention to chemistry principally under the direction of Professor F. H. Storer.

In 1870 he became chemist of the Merrimack Print Works at Lowell, and, while holding this position, introduced successfully a process for recovering alizarine from the spent residues of the madder root by the use of sulphuric acid, which was new to this country, — a remarkable achievement for a young man of twenty-two. It is striking to note that even as a beginner he was not content with the mere routine work of his position, but entered at once the field in which he was destined to reap such abundant harvests, for his principal merit lies in making effective, on a commercial scale, new processes, whether of his own invention or foreign ones as yet unknown in America. This adaptation of foreign processes is not by any means the simple matter which it might appear at first sight; great judgment is necessary in selecting the one best fitted to the needs of this country, and, after this is done.

the details must in many cases be reinvented, or, when not carefully guarded secrets, they usually need extensive modifications to fit them to American conditions, which differ in many and unexpected ways from those abroad. It would be a mistake, however, to suppose from this early success that he was a precocious genius, who leaped to results by some intuitive process; on the contrary, his mind moved rather slowly, and his early successes were obtained by patient, well-directed, persistent labor.

In 1873 he went to Europe to complete his chemical education, and studied for the first half year with Emil Kopp, in the Zürich Polytechnicum, where he gave part of his time to the analysis of aniline black, a dyestuff then recently introduced. The second half of the year was devoted to travel, and especially to visits to laboratories and chemical works. At this time he was only twenty-four years old, but it was striking to see the most eminent chemists receiving him as a fellow-chemist, and discussing scientific matters with him as with a contemporary. The acquaintanceships made at this time, and the practical knowledge acquired, were of life-long value to him.

In 1874, after his return to America with greater attainments and enlarged horizons, he attempted to establish at the Lowell Bleachery the Solvay process for making sodic carbonate, then only eleven years old, but without success. This is an excellent example of the difficulties in introducing foreign manufacturing processes. There was no lack of judgment in the selection of the process, as is shown by the enormous development of it at Syracuse, where it was started under the auspices of the mother company in Belgium ten years later; the details also seemed to be sufficiently well known, but the working out of these details so as to secure success needed not only the highest ability of the technical chemist, but also mechanical engineering of a most difficult and unusual sort, which at that time was beyond him. His failure, therefore, was not surprising or mortifying, and he had the happy faculty of learning from his failures, and, like Peter the Great, making them the school for later victories. After this he spent a short time in the office of his uncle, Henry Lee, learning business methods.

His only chemical papers date from this period, 1872–1877. They are seven in number and of good quality for a beginner, but he evidently soon realized that the publication of original researches was not his line of work, since he could be employed much more usefully for the community and himself in perfecting chemical manufactures. With this end in view he became the most expert consulting chemist for industrial work in this part of the country, and continued to give advice

of this sort, as he could find time, until his own manufactures absorbed his whole attention.

It was in 1877 that he began business on his own account in partnership with Frederick Nourse. They established a coal-tar distillery at Chelsea, from which he hoped to develop an industry in fine organic chemicals similar to that which was then showing such wonderful growth in Germany, but the time was not ripe for such a growth in America; in fact, even now, thirty years afterward, this industry has not yet emerged from its infancy. Accordingly he turned his attention to the less varied list of products for which he found a demand. Among these, lampblack was the most important, and he at once improved the apparatus for its manufacture in his usual thorough, painstaking way. Mr. Nourse retired from the partnership in the autumn of 1878, and after this he had sole charge of the business, keeping himself a firm grasp on all departments of it, with the assistance of a series of able managers, — his brother-in-law, Mr. C. P. Nichols, Mr. Edward Cunningham, Mr. W. R. Cabot, and Mr. M. G. Bennett.

Always on the lookout for new fields of work, his attention was called at an early day to the gas region of Pennsylvania, in which he hoped to find mineral wealth similar to that of the Midland region of England. Although these hopes were not fulfilled, the investigation led him to the establishment in 1882–1883 of a plant at Worthington, Pennsylvania, for making carbon black by burning natural gas against a cast-iron plate beneath which the burner and black-box revolved. This method, which was in part, perhaps wholly, original with him, is still in use in the largest factory for this product. After a few years, however (in 1888), his brother, Godfrey L. Cabot, who had worked with him for a short time, took this business off his hands, and has carried it on successfully ever since.

At about the same time he began the manufacture of sulpho-naphthol—one of the most excellent disinfectants known; and another profitable new industry, rendered effective by him somewhat later, was the preparation of creosote shingle stains. Many attempts had been made in foreign countries to use creosote as a basis for paint, but none of these had been crowned with success. He, however, had the penetration to see that such a paint or stain would be specially adapted for use with shingles, which were essentially unknown abroad, and after this a painstaking study of the details and great care and thoroughness in the manufacture led to a complete victory over the difficulties, which had proved too much for his predecessors. His insulating felt for deadening sound, keeping out cold, and fireproofing, was an entirely original idea. It consisted of eel-grass quilted between two

layers of asbestos or felting, and proved especially well adapted for these purposes, thus furnishing a use for a very cheap and hitherto worthless material.

Not every experiment was a success, however; as with all inventors, his path was strewn with failures, for it was not enough to make a process work, but it must also pay. Thus, for instance, he invented a set of stains on a creosote basis for interior use in houses, but, although admirable from the technical and artistic standpoints, the demand for them was so small that it was not worth while to manufacture them.

At the time of his death his principal products were shingle-stains, lampblack, deadening-felt, sulpho-naphthol, benzol, naphtha, brick preservative, sheep dip, mortar colors, black varnish, and coal-tar pitch. I give this list to show how far he had departed from his original plan of establishing a varied manufacture of fine chemicals, as it seems to me a remarkable proof of his sagacity that he was able to select products for which there was a demand, instead of wasting his energies on lines of work for which the country was not prepared.

One of his most interesting achievements was the successful establishment of a system of profit-sharing with the operatives of his factory. I am fortunately able to give an account of it in his own words, taken from an address on the subject delivered a few years ago before the American Social Science Association.

"At a very early period in my business experience it appeared to me that the rewards ordinarily offered to the wage-earner were not such as to stimulate him to the best exertion nor foster in him the best and kindest feelings toward his employer.

"Even to-day is it not true that in the great majority of cases the wage-earner's only stimulus is the desire to hold his job? In fact, is not the fear of discharge the only incentive to exertion in a large majority of cases?

"Feeling as I did, and still do, that men can always be led more successfully than they can be driven, that Hope as leader and captain can accomplish more than Fear as tyrant and slave-driver, I set myself—ignorantly and crudely to be sure, but earnestly—to try to do better things. My method has grown to be essentially as follows:

"Every man who enters my employ is given the current rate of wages for similar work. If he desires also to participate in the profit-sharing, he is required to sign a paper in which he promises to do his work as quickly and carefully as possible, remembering that the greater the yield the larger the profits, and to give me sixty days' notice before leaving me.

"On my part, I promise to divide, at the expiration of each six

months, a certain fraction of the profits among the participants, strictly in proportion to the wages of each during that period. This sum in each case is divided into two equal parts, one of which is given in cash to the employee and the other is deposited in a savings-bank by me as his trustee.

"This fund in the bank is in the nature of an insurance upon the life of the employee, and is given over with interest to his executors, if he dies. It, however, does not come back into my hands. If he should, for instance, refuse to give me sixty days' notice on leaving me, although he had already received an equal amount in cash upon the promise to give me such notice, the money would not come back to me, but would simply be distributed among the other participants at the next division.

"The same is true in case of his discharge for cause.

"In case of sickness I am empowered at my discretion to draw upon his fund, though in temporary cases I always put sick men on halfpay for a considerable time without recourse to their fund. I also have the right to lend him money upon it to build a house. And now

let me give you a few figures.

"The system was begun a little over seventeen years ago, and has gone on uninterrupted up to the present time. The profit-sharers at the outset numbered 21, and to-day number 42. The total amount paid out by me has been \$40,464 during that period. Now the natural question which you all will ask, I think, is, Has this been a good bargain? I think you will all agree that in the ultimate analysis no bargain is a good bargain that is not profitable to both sides. Well, there will, I think, be no dispute that from the workman's point of view the bargain has been a good one, as he has a very considerable addition to his wages, which were as high as other labor of the same kind; and I may say that the average wages have steadily advanced as the efficiency and skill increased.

"But now comes the question of my own investment: What means have I of knowing that the efficiency of the workmen has been increased to an amount equivalent to the \$40,464 which I have

expended?

"I will now give you a few more statistics which bear upon this question. Let me remind you that the same proportion of the profit was paid to the 21 men who first entered the agreement that is now paid to the 42 men who compose the present corps. But now note this very significant fact. While the first payments averaged about 10 per cent upon the wages of each man, the last payment — which was larger than usual, to be sure — was exactly  $21_{130}^{-1}$  per cent of their wages.

"It seems to me obvious that, if we can draw any inference from these facts, it is that, inasmuch as my profit compared to the wages paid has increased, the efficiency of my workmen has improved.

"But, above all, my own observation has convinced me that the morale of my employees is much superior to the average, and that they are more contented and willing by far than is usual in similar establishments. In fact, I am satisfied that this bargain has been a good bargain, a good one for both parties to it, and that the extra money I have laid out has been well and profitably invested.

"I have, for obvious reasons, not laid any emphasis upon the philanthropic side of this enterprise, especially as I am sure it can be recommended to many, if not to most, manufacturers, and to their employees, purely upon its utilitarian advantages; but it is obvious that it stimulates both sobriety and thrift in workmen, and that it can be made to assist men of family to build homes for themselves, thus surrounding the factory with the homesteads of men who are interested in its success and that of the neighborhood.

"From my seventeen years' experience, therefore, gentlemen, I can cordially recommend profit-sharing on this or a similar plan as of marked advantage to both employer and employed."

I have quoted this paper almost entire, because it seems to me to show the man — his desire for the good of others, joined to sound business common sense, and the practical wisdom needed to make the scheme effective. That it was effective is shown by the fact that, when a new hand was inclined to be indolent, the other workmen insisted on vigorous work from him if he was to stay in the factory, for, said they, "We will not have our profits cut down by the lazy or inefficient." It will be observed that the success of this system depended on an absolute trust on the part of the men in the uprightness of their employer. The slightest suspicion that it would not be carried out equitably, or that in some underhand way it would redound to the profit of the chief, would have wrecked it at once. And here the comparatively small number of men was a potent factor, as they were all able to know Mr. Cabot personally, and to realize his absolute honesty and fairness. That they also learned to love him appeared from the impressive sorrow with which they attended his funeral.

This absolute honesty and fairness was also conspicuous in his business relations. He would often make concessions beyond what could be justly demanded, if he thought the claim was made in good faith, while, on the other hand, he would not yield an inch when this was not the case, but proved a dangerous and pertinacious adversary. In one case at a very early stage in his career a man who had circulated

malicious stories about his goods was forced to sign a written retraction couched in the most abject terms.

His business activities would have been enough to exhaust the energy of most men, but he found time and strength for the enthusiastic pursuit of many other interests. He was a most devoted son of the Institute of Technology, always ready with advice or more material help. In 1889 he was elected to the Corporation intrusted with its government, and in spite of his strong opinions and fighting blood won and kept the respect and affection of all his fellow-members. He was a member of the executive committee for many years, and very active on committees in charge of special departments, serving at various times on those on chemistry, chemical engineering, physics, botany, biology, modern languages, and English. His principal interest was naturally in the Chemical Department, which he watched over with unceasing care. He even induced Professor Lunge to come to Boston from Zürich to examine it, and make suggestions in regard to the best methods for teaching industrial chemistry.

Nor did he confine his attention to the Institute of Technology, as for many years he was a member of the "Committee to visit the Chemical Laboratory" of Harvard University, and in this capacity gave much useful advice about the organization of the course in industrial chemistry, in which he advocated the teaching of broad general principles rather than instruction in details, showing in this way a power of rising above the narrowing tendency of the highly specialized work by which alone a chemical manufacturer attains success.

He was devoted to athletics throughout his life, telling with gusto in one of his last years how he had beaten a much younger man at tennis, and about the same time causing the publication of a delightful volume of reminiscences by the idol of his boyhood, Lovett, the pitcher of the Lowells. This interest influenced his relations with the Institute of Technology, as he was a member of the Advisory Council on Athletics, and gave a tract of land in Brookline for a playground. He also established an annual prize for the greatest improvement in athletics, and gave a silver cup, on which the names of the victors were inscribed each year. It is almost needless to add that his influence was always used in maintaining the highest ideal of sportsmanship. In addition to these gifts for athletics he gave his house in Brookline for a dormitory, and was always ready to answer any pressing need.

He threw himself with the same enthusiasm into other recreations. Thus he made a careful study of the theory and construction of aeroplanes, for many years carrying on experiments in the summer on kites, studying especially the resistance of the air to various forms, and the

effect of atmospheric currents. While in Europe in 1896 he saw Maxim and Lilienthal, and provided the latter with money to carry on his work; and in this country he stood ready to help the Wright brothers, when the time should come to make their experiments public.

Another engrossing pursuit was the study of the authorship of the plays of Shakespeare. He espoused the Baconian theory with great vigor, and defended his position by elaborate and costly investigations. His fine taste for art made him an authority on this subject also, and proved of great use to him in some of the branches of his business.

He was elected a fellow of our Academy in 1893, and served on the C. M. Warren Committee from its establishment in the same year until his death. That he held no other office was from his own choice, since he was at one time elected treasurer of the Academy, but declined to serve. He was also a member of the Society for Chemical Industry.

In 1878 he married Helen Augusta Nichols, of Lowell, and they had two children, a daughter and a son. In his family and society his genial, affectionate nature won all hearts. It made one happier for the whole day simply to exchange a few words with him in the street.

This life, so full of various beneficent activities, was brought to an end by a sudden attack of pneumonia, November 26, 1906.

In looking back at his life the most striking characteristic was, I think, his very high standards. It was not enough that he should be successful from a worldly point of view, but in all his undertakings the good of the country was a prime consideration; the introduction of new and useful processes, the utilization of waste materials, were his objects quite as much as his own personal advantage. Further, all his products must be of the highest quality, all his processes brought to the highest perfection. His probity was without a flaw, and anything mean or underhanded aroused in him a scorching, disdainful wrath, — for he was always a fighter, never afraid of an outspoken expression of his opinion; yet even in his more vehement controversies his antagonists could never lose sight of his sincerity of purpose and his large, warm With all his vehemence of opinion his character was a singularly gentle and affectionate one, so that his genial nature won the love of all who knew him well. His thoroughness in all his pursuits, and the good judgement with which he selected or abandoned his manufacturing experiments, have been dwelt on sufficiently in the narrative of his life; but not enough has been said there of his generosity — always on the watch to help the deserving, yet concealed so carefully that in one case at least even the person benefited did not know from whom the help had come. To these he added a modesty and humility which led him always to undervalue his ability and attainments, a purity so feminine that it was respected even by the wilder men whom he chanced to encounter in his youth, and a strong and vivid imagination both in his experiments and recreations.

His ruddy face under a mass of curly hair always beamed with a genial light; and he seemed to glow with exuberant life and enthusiasm while he discussed some important subject in a slow rather hesitating manner, as if his abundant ideas found difficulty in gaining utterance. It seems impossible to believe that this overflowing vitality is no longer with us.

CHARLES LORING JACKSON.

# American Academy of Arts and Sciences OFFICERS AND COMMITTEES FOR 1908-09.

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VICE-PRESIDENT.

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Class II. HENRY P. WALCOTT,

Class III. JOHN C. GRAY.

CORRESPONDING SECRETARY.

EDWIN H. HALL.

RECORDING SECRETARY.

WILLIAM WATSON.

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Terms extire 1909.

JOHN E. WOLFF, GEORGE L. KITTREDGE.

Terms extire 1910.

WILLIAM L. HOOPER,

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# LIST

OF THE

## FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to June 1, 1908.)

## RESIDENT FELLOWS. - 189.

(Number limited to two hundred.)

Class I. — Mathematical and Physical Sciences. — 78.

## SECTION I. - 14.

Mathematics and Astronomy.

| Solon I. Bailey,       | Cambridge.     |
|------------------------|----------------|
| Maxime Bôcher,         | Cambridge.     |
| William E. Byerly,     | Cambridge.     |
| Seth C. Chandler, W    | ellesley Hills |
| Percival Lowell,       | Boston.        |
| Edward C. Pickering,   | Cambridge.     |
| William II. Pickering, | Cambridge.     |
| John Ritchie, Jr.,     | Dorchester.    |
| Arthur Searle,         | Cambridge.     |
| William E. Story,      | Worcester.     |
| Henry Taber,           | Worcester.     |
| Harry W. Tyler,        | Boston.        |
| O. C. Wendell,         | Cambridge.     |
| P. S. Yendell,         | Dorchester.    |

## SECTION II. - 27.

## Physics.

A. Graham Bell, Washington, D.C.
Louis Bell, Boston.
Clarence J. Blake, Boston.
Francis Blake, Weston.
George A. Campbell, New York.
Harry E. Clifford. Newton.
Charles R. Cross, Brookline.
Louis Derr, Brookline.

| A. W. Duff,         | Worcester.  |
|---------------------|-------------|
| II. M. Goodwin,     | Roxbury.    |
| Edwin H. Hall,      | Cambridge.  |
| Hammond V. Hayes,   | Cambridge.  |
| William L. Hooper,  | Somerville. |
| William W. Jacques, | Newton.     |
| Frank A. Laws,      | Boston.     |
| Henry Lefavour,     | Boston.     |
| Theodore Lyman,     | Brookline.  |
| Charles L. Norton,  | Boston.     |
| Benjamin O. Peirce, | Cambridge.  |
| George W. Pierce,   | Cambridge.  |
| A. Lawrence Rotch,  | Boston.     |
| Wallace C. Sabine,  | Boston.     |
| John S. Stone,      | Boston.     |
| Elihu Thomson,      | Swampscott  |
| John Trowbridge,    | Cambridge.  |
| A. G. Webster,      | Worcester.  |
| Robert W. Willson,  | Cambridge.  |
|                     |             |

#### Section III. - 19.

#### Chemistry.

| Gregory Paul I  | axter, Cambridge. |
|-----------------|-------------------|
| Arthur M. Con   | ney, Cambridge.   |
| James M. Craf   | ts, Boston.       |
| Charles W. Eli  | ot, Cambridge.    |
| Charles L. Jack | sson, Cambridge.  |
| Walter L. Jeni  | ings, Worcester.  |

Leonard P. Kinnicutt, Worcester. Charles F. Mabery, Cleveland, O. George D. Moore, Worcester. James F. Norris, Boston. Arthur A. Noves, Boston. Robert H. Richards, Jamaica Plain. Theodore W. Richards, Cambridge. Cambridge. Charles R. Sanger, Stephen P. Sharples, Cambridge. Francis II. Storer, Boston. Henry P. Talbot, Newton. William H. Walker, Newton. Charles II. Wing, Boston.

## SECTION IV. - 18.

Technology and Engineering.
Comfort A. Adams, Cambridge.

Alfred E. Burton. Boston. Eliot C. Clarke, . Boston. Heinrich O. Hofman, Jamaica Plain. Ira N. Hollis, Cambridge. L. J. Johnson, Cambridge. Arthur E. Kennelly, Cambridge. Boston. Gaetano Lanza, E. D. Leavitt. Cambridge. William R. Livermore, New York. Lowell. Hiram F. Mills, Brookline. Cecil H. Peabody, Paris. Andrew H. Russell, Albert Sauveur. Cambridge. Peter Schwamb, Arlington. H. L. Smyth, Cambridge. George F. Swain. Boston. William Watson, Boston.

## Class II. — Natural and Physiological Sciences. — 59.

#### SECTION I. - 16.

Geology, Mineralogy, and Physics of the Globe.

H. H. Clayton, Milton. Algernon Coolidge, Boston. William O. Crosby, Jamaica Plain. William M. Davis, Cambridge. Benj. K. Emerson, Amherst. O. W. Huntington, Newport, R. I. Robert T. Jackson, Cambridge. T. A. Jaggar, Jr., Cambridge. Cambridge. Douglas W. Johnson, William H. Niles, Cambridge. Charles Palache, Cambridge. Washington. John E. Pillsbury, Robert DeC. Ward, Cambridge. Auburndale. Charles H. Warren, Cambridge. John E. Wolff. Cambridge. J. B. Woodworth,

## Section II. - 11.

## Botany.

F. S. Collins, Malden. William G. Farlow. Cambridge. Charles E. Faxon. Jamaica Plain. Merritt L. Fernald. Cambridge. George L. Goodale, Cambridge. Jamaica Plain. John G. Jack. Edward C. Jeffrey, Cambridge. B. L. Robinson, Cambridge. Brookline. Charles S. Sargent, Arthur B. Seymour, Cambridge. Cambridge. Roland Thaxter,

#### Section III. -21.

Zoölogy and Physiology.

Alexander Agassiz, Cambridge. Robert Amory, Boston.

Henry P. Bowditch, William Brewster, Cambridge. Brookline. Louis Cabot. Walter B. Cannon, Cambridge. William E. Castle, Cambridge. Samuel F. Clarke. Williamstown. W. T. Conneilman, Boston. Harold C. Ernst. Jamaica Plain Samuel Henshaw, Cambridge. Cambridge. Edward L. Mark, Charles S. Minot, Milton. Edward S. Morse, Salem. George H. Parker. Cambridge. William T. Porter, Boston. James J. Putnam. Boston. Samuel H. Scudder. Cambridge. William T. Sedgwick, Boston.

Jamaica Plain. James C. White, Boston. Cambridge. William M. Woodworth, Cambridge.

#### SECTION IV. - 11.

Medicine and Surgery.

Edward H. Bradford, Boston. Arthur T. Cabot. Boston. Reginald H. Fitz, Boston. Frederick I. Knight, Boston. Samuel J. Mixter, Boston. W. L. Richardson. Boston. Theobald Smith. Jamaica Plain. O. F. Wadsworth, Boston Henry P. Walcott, Cambridge. John C. Warren. Boston. Francis H. Williams, Boston,

## Class III. — Moral and Political Sciences. — 52.

#### SECTION I. - 8.

Philosophy and Jurisprudence.

James B. Ames, Cambridge. Joseph H. Beale. Jr., Cambridge. John C. Gray, Boston. Francis C. Lowell, Boston. Huzo Münsterberg. Cambridge. Cambridge. Josiah Royce, Dedham. Frederic J. Stimson. Samuel Williston. Belmont.

## SECTION II. - 19.

Philology and Archaeology.

Charles P. Bowditch, Jamaica Plain. Lucien Carr, Cambridge.

Franklin Carter, Williamstown. J. W. Fewkes, Washington. William W. Goodwin. Cambridge. Henry W. Haynes, Boston. Albert A. Howard. Cambridge. Charles R. Lanman, Cambridge. David G. Lyon, Cambridge. George F. Moore, Cambridge. Morris H. Morgan, Cambridge. Frederick W. Putnam, Cambridge. Edward Robinson. New York. Edward S. Sheldon, Cambridge. Herbert Weir Smyth, Cambridge. F. B. Stephenson, Boston. Crawford H. Toy, Cambridge. John W. White. Cambridge. John H. Wright, Cambridge.

## Section III. - 12.

# Political Economy and History.

#### Charles F. Adams, Lincoln. Thomas N. Carver, Cambridge. Andrew McF. Davis, Cambridge. Ephraim Emerton, Cambridge. A. C. Goodell, Salem. Charles Gross, Cambridge. Henry C. Lodge, Nahant. A. Lawrence Lowell, Boston. James F. Rhodes. Boston. William Z. Ripley, Newton. Charles C. Smith, Boston. F. W. Taussig, Cambridge.

#### SECTION IV. - 13.

## Literature and the Fine Arts.

| Francis Bartlett,     | Boston.    |
|-----------------------|------------|
| Arlo Bates,           | Boston.    |
| L. B. R. Briggs,      | Cambridge. |
| Kuno Francke,         | Cambridge. |
| Edward H. Hall,       | Cambridge. |
| T. W. Higginson,      | Cambridge. |
| George L. Kittredge,  | Cambridge. |
| William C. Lane,      | Cambridge, |
| Charles Eliot Norton, | Cambridge. |
| Denman W. Ross,       | Cambridge. |
| William R. Ware,      | Milton.    |
| Herbert L. Warren,    | Cambridge. |
| Barrett Wendell,      | Boston.    |

## ASSOCIATE FELLOWS. - 92.

(Number limited to one hundred. Elected as vacancies occur.)

## Class I. — Mathematical and Physical Sciences. — 36.

SECTION I. — 12.

Mathematics and Astronomy.

Edward E. Barnard, Williams Bay, Wis.

S. W. Burnham, Williams Bay, Wis. George Davidson, San Francisco. Fabian Franklin, Baltimore. George W. Hill, W. Nyack, N.Y.

E. S. Holden, New York.
Emory McClintock, Morristown, N.J.
E. H. Moore, Chicago.

Simon Newcomb, Washington.
Charles L. Poor, New York.
George M. Searle, Washington.

J. N. Stockwell, Cleveland, O.

Section II. — 6.

Physics.

Carl Barus, Providence, R.I.
G. E. Hale, Williams Bay, Wis.
T. C. Mandenbell, Worcest v.

T. C. Mendenhall, Worcester. A. A. Michelson, Chicago.

E. L. Nichols, Ithaca. N. Y.

M. I. Pupin, New York.

Section III.  $\rightarrow$  10.

Chemistry.

Wolcott Gibbs, Newport, R.I. Frank A. Gooch, New Haven.

Eugene W. Hilgard, Berkeley, Cal. S. W. Johnson, New Haven.

J. W. Mallet, Charlottesville, Va.

E. W. Morley, W. Hartford, Conn.

Charles E. Munroe, Washington.

John U. Nef, Chicago, Ill. J. M. Ordway, New Orleans.

Ira Remsen, Baltimore.

SECTION IV. — 8.

Technology and Engineering.

Henry L. Abbot, Cambridge.
Cyrus B. Comstock, New York. [Va.
W. P. Craighill, Charlestown, W.

John Fritz. Bethlehem, Pa.

James D. Hague, New York. F. R. Hutton, New York.

F. R. Hutton, New York.
William Sellers, Edge Moor, Del.

Robt. S. Woodward, Washington.

## Class II. - Natural and Physiological Sciences. - 32.

Section I. - 9.

Geology, Mineralogy, and Physics of Walter G. Davis, the Globe. Samuel F. Emmo

Cleveland Abbe, Washington.
George J. Brush, New Haven.

T. C. Chamberlin, Chicago.Edward S. Dana, New Haven.

Walter G. Davis, Cordova, Arg. Samuel F. Emmons, Washington.
G. K. Gilbert, Washington.

R. Pumpelly, Newport, R.I. Charles D. Walcott, Washington.

# Section II. — 6. Botany.

L. H. Bailey,
D. H. Campbell,
J. M. Coulter,
C. G. Pringle,
John D. Smith,
W. Trelease,
Uthaca, N. Y.
Palo Alto, Cal.
Chicago.
Charlotte, Vt.
Baltimore.
W. Louis.

#### Section III. - 9.

Zoölogy and Physiology.

Joel A. Allen, New York,
W. K. Brooks, Lake Roland, Md.
C. B. Davenport,

Cold Spring Harbor, N. Y. F. P. Mall, Baltimore.

| S. Weir Mitchell, | Philadelphia. |
|-------------------|---------------|
| H. F. Osborn,     | New York.     |
| A. E. Verrill,    | New Haven.    |
| C. O. Whitman,    | Chicago.      |
| E. B. Wilson,     | New York.     |

#### SECTION IV. - 8.

Medicine and Surgery.

John S. Billings, New York.
W. S. Halsted, Baltimore.
Abraham Jacobi, New York.
W. W. Keen, Philadelphia.
William Osler, Baltimore.
T. Mitchell Prudden, New York.
Wm. H. Welch, Baltimore.
H. C. Wood, Philadelphia.

## Class III. — Moral and Political Sciences. — 24.

#### Section I. -6.

Philosophy and Jurisprudence.

Joseph H. Choate, New York.
Melville W. Fuller, Washington.
William W. Howe, New Orleans.
Charles S. Peirce, Milford, Pa.
G. W. Pepper, Philadelphia.
T. R. Pynchon, Hartford, Conn.

#### Section II. - 6.

Philology and Archwology.

Timothy Dwight, New Haven.
B. L. Gildersleeve, Baltimore.
D. C. Gilman, Baltimore.
T. R. Lounsbury, New Haven.
Rufus B. Richardson, New York.
A. D. White, Ithaca, N.Y.

#### Section III. - 7.

Political Economy and History.

Henry Adams,
G. P. Fisher.
Arthur T. Hadley,
Henry C. Lea,
Alfred T. Mahan,
H. Morse Stephens,
W. G. Sumner,
Washington.
New Haven.

#### SECTION IV. - 5.

Literature and the Fine Arts.

James B. Angell,
H. H. Furness,
R. S. Greenough,
Herbert Putnam,
John S. Sargent,
London.

Ann Arbor, Mich.
Wallingford, Pa.
Washington.
London.

#### FOREIGN HONORARY MEMBERS. - 65.

(Number limited to seventy-five. Elected as vacancies occur.)

Class I. — Mathematical and Physical Sciences. — 20.

#### Section I. — 6.

Mathematics and Astronomy.

Arthur Auwers, Berlin.
George H. Darwin, Cambridge.
Sir William Huggins, London.

Felix Klein, Göttingen. Émile Picard, Paris. II. Poincaré, Paris.

## Section II. - 5.

## Physics.

Oliver Heaviside, Newton Abbot.
F. Kohlrausch, Marburg,
Joseph Larmor, Cambridge.
Lord Rayleigh, Witham.
Joseph J. Thomson, Cambridge.

#### SECTION III. - 6.

#### Chemistry.

Adolf Ritter von Baeyer, Munich.
Emil Fischer, Berlin.
J. H. van't Hoff, Berlin.
Wilhelm Ostwald, Leipsic.
Sir H. E. Roscoe, London.
Julius Thomsen, Copenhagen.

#### SECTION IV. - 3.

Technology and Engineering.

Maurice Lévy, Paris. II. Müller-Breslau, Berlin. W. Cawthorne Unwin, London.

## Class II.—Natural and Physiological Sciences.—22.

#### Section I. - 4.

# Geology, Mineralogy, and Physics of

the Globe.

Sir Archibald Geikie, London.
Julius Hann, Vienna.
Albert Heim, Zurich.
Sir John Murray, Edinburgh.

## SECTION II. - 6.

#### Botany.

E. Bornet, Paris.
A. Engler, Berlin.
Sir Joseph D. Hooker, Sunningdale.
W. Pfeffer, Leipsic.
H. Graf zu SolmsLaubach, Strassburg.
Eduard Strasburger, Bonn.

#### SECTION III. - 5.

# Zoölogy and Physiology.

Ludimar Hermann, Königsberg.
H. Kronecker, Bern.
E. Ray Lankester, London.
Elias Metschnikoff, Paris.
M. Gustay Retzius, Stockholm.

#### SECTION IV. -7.

## Medicine and Surgery.

Emil von Behring, Marburg.
Sir T. L. Brunton, London.
A. Celli, Rome.
Sir V. A. H. Horsley, London.
R. Koch, Berlin.
Lord Lister, London.
F. v. Recklinghausen, Strassburg.

## Class III. - Moral and Political Sciences. - 23.

#### Section I. - 5.

## Philosophy and Jurisprudence.

A. J. Balfour, Prestonkirk.
Heinrich Brunner, Berlin.
A. V. Dicey, Oxford.
F. W. Maitland, Cambridge.
Sir Frederick Pollock,
Bart., London.

#### Section II. -7.

## Philology and Archæology.

Ingram Bywater,
F. Delitzsch,
Hermann Diels,
W. Dörpfeld,
Sir John Evans,
H. Jackson,
G. C. C. Maspero,
Paris.
Oxford.
Berlin.
Athens.
Berkhampsted.
Cambridge.

## SECTION III. - 5.

## Political Economy and History.

James Bryce. London.
Adolf Harnack, Berlin.
Sir G. O. Trevelyan,
Bart., London.
John Morley, London.
Pasquale Villari, Florence.

#### SECTION IV. - 6.

#### Literature and the Fine Arts.

E. de Amicis, Turin.
Gaston Boissier, Paris.
Georg Brandes, Copenhagen.
S. H. Butcher, London.
Jean Léon Gérôme, Paris.
Rudyard Kipling, Burwash.

# STATUTES AND STANDING VOTES.

# STATUTES.

Adopted May 30, 1854: amended September 8, 1857, November 12, 1862,
May 24, 1864, November 9, 1870, May 27, 1873, January 26, 1876,
June 16, 1886, October 8, 1890. January 11, and May 10, 1893, May 9, and October 10, 1894, March 13, April 10, and May 8, 1895, May 8, 1901, January 8, 1902, May 10, 1905, February 14 and March 14, 1906.

## CHAPTER I.

## OF FELLOWS AND FOREIGN HONORARY MEMBERS.

- 1. The Academy consists of Resident Fellows, Associate Fellows, and Foreign Honorary Members. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, viz.: Class I. The Mathematical and Physical Sciences; Class II. The Natural and Physiological Sciences; Class III. The Moral and Political Sciences. Each Class is divided into four Sections, viz.: Class I., Section 1. Mathematics and Astronomy; Section 2. Physics; Section 3. Chemistry; Section 4. Technology and Engineering. Class II., Section 1. Geology, Mineralogy, and Physics of the Globe; Section 2. Botany; Section 3. Zoölogy and Physiology; Section 4. Medicine and Surgery. Class III., Section 1. Theology, Philosophy, and Jurisprudence; Section 2. Philology and Archaeology; Section 3. Political Economy and History; Section 4. Literature and the Fine Arts.
- 2. The number of Resident Fellows residing in the Commonwealth of Massachusetts shall not exceed two hundred, of whom there shall not be more than eighty in any one of the three classes. Only residents in the Commonwealth of Massachusetts shall be eligible to election as Resident Fellows, but resident fellowship may be retained after removal from

the Commonwealth. Each Resident Fellow shall pay an admission fee of ten dollars and such annual assessment, not exceeding ten dollars, as shall be voted by the Academy at each annual meeting. Resident Fellows only may vote at the meetings of the Academy.

- 3. The number of Associate Fellows shall not exceed one hundred, of whom there shall not be more than forty in either of the three classes of the Academy. Associate Fellows shall be chosen from persons residing outside of the Commonwealth of Massachusetts. They shall not be liable to the payment of any fees or annual dues, but on removing within the Commonwealth they may be transferred by the Council to resident fellowship as vacancies there occur.
- 4. The number of Foreign Honorary Members shall not exceed seventy-five; and they shall be chosen from among persons most eminent in foreign countries for their discoveries and attainments in either of the three departments of knowledge above enumerated. There shall not be more than thirty Foreign Members in either of these departments.

## CHAPTER II.

#### OF OFFICERS.

- 1. There shall be a President, three Vice-Presidents, one for each Class, a Corresponding Secretary, a Recording Secretary, a Treasurer, and a Librarian, which officers shall be annually elected, by ballot, at the annual meeting, on the second Wednesday in May.
- 2. There shall be nine Councillors, chosen from the Resident Fellows. At each annual meeting, three Councillors shall be chosen, by ballot, one from each Class, to serve for three years; but the same Fellow shall not be eligible for two successive terms. The nine Councillors, with the President, the three Vice-Presidents, the two Secretaries, the Treasurer, and the Librarian, shall constitute the Council. Five members shall constitute a quorum. It shall be the duty of this Council to exercise a discreet supervision over all nominations and elections. With the consent of the Fellow interested, they shall have power to make transfers between the several sections of the same Class, reporting their action to the Academy.
- 3. The Council shall at its March Meeting receive reports from the Rumford Committee, the C. M. Warren Committee, the Committee on Publication, the Committee on the Library, the President and Record-

ing Secretary, and the Treasurer, proposing the appropriations for their work during the year beginning the following May. The Treasurer at the same meeting shall report on the income which will probably be received on account of the various Funds during the same year.

At the Annual Meeting, the Council shall submit to the Academy, for its action, a report recommending the appropriations which in the opinion of the Council should be made for the various purposes of the Academy.

4. If any office shall become vacant during the year, the vacancy shall be filled by a new election, at the next stated meeting, or at a meeting called for this purpose.

#### CHAPTER III.

#### OF NOMINATIONS OF OFFICERS.

- 1. At the stated meeting in March, the President shall appoint a Nominating Committee of three Resident Fellows, one for each Class.
- 2. It shall be the duty of this Nominating Committee to prepare a list of candidates for the offices of President, Vice-Presidents, Corresponding Secretary, Recording Secretary, Treasurer, Librarian, Councillors, and the Standing Committees which are chosen by ballot; and to cause this list to be sent by mail to all the Resident Fellows of the Academy not later than four weeks before the Annual Meeting.
- 3. Independent nominations for any office, signed by at least five Resident Fellows, and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted in the call for the Annual Meeting, which shall then be issued not later than one week before that meeting.
- 4. The Recording Secretary shall prepare for use, in voting at the Annual Meeting, a ballot containing the names of all persons nominated for office under the conditions given above.
- 5. When an office is to be filled at any other time than at the Annual Meeting, the President shall appoint a Nominating Committee in accordance with the provisions of Section 1, which shall announce its nomination in the manner prescribed in Section 2 at least two weeks before the time of election. Independent nominations, signed by at least five Resident Fellows and received by the Recording Secretary not later than one week before the meeting for election, shall be inserted in the call for that meeting.

#### CHAPTER IV.

## OF THE PRESIDENT.

- 1. It shall be the duty of the President, and, in his absence, of the senior Vice-President present, or next officer in order as above enumerated, to preside at the meetings of the Academy; to direct the Recording Secretary to call special meetings; and to execute or to see to the execution of the Statutes of the Academy. Length of continuous membership in the Academy shall determine the seniority of the Vice-Presidents.
- 2. The President, or, in his absence, the next officer as above enumerated, shall nominate members to serve on the different committees of the Academy which are not chosen by ballot.
- 3. Any deed or writing to which the common seal is to be affixed shall be signed and sealed by the President, when thereto authorized by the Academy.

#### CHAPTER V.

## OF STANDING COMMITTEES.

- 1. At the Annual Meeting there shall be chosen the following Standing Committees, to serve for the year ensuing, viz.:—
- 2. The Committee on Finance to consist of three Fellows to be chosen by ballot, who shall have, through the Treasurer, full control and management of the funds and trusts of the Academy, with the power of investing and of changing the investment of the same at their discretion.
- 3. The Rumford Committee, to consist of seven Fellows to be chosen by ballot, who shall consider and report to the Academy on all applications and claims for the Rumford premium. They shall also report to the Council in March of each year on all appropriations of the income of the Rumford Fund needed for the coming year, and shall generally see to the due and proper execution of the trust. All bills incurred on account of the Rumford Fund, within the limits of the appropriation made by the Academy, shall be approved by the Chairman of the Rumford Committee.
- 4. The C. M. Warren Committee, to consist of seven Fellows to be chosen by ballot, who shall consider and report to the Council in March of each year on all applications for appropriations from the income of the C. M. Warren Fund for the coming year, and shall generally see to the due

and proper execution of the trust. All bills incurred on account of the C. M. Warren Fund, within the limits of the appropriations made by the Academy, shall be approved by the Chairman of the C. M. Warren Committee.

- 5. The Committee on Publication to consist of three Fellows, one from each class, to whom all communications submitted to the Academy for publication shall be referred, and to whom the printing of the Proceedings and Memoirs shall be entrusted. This Committee shall report to the Council in March of each year on the appropriations needed for the coming year. All bills incurred on account of publications, within the limits of the appropriations made by the Academy, shall be approved by the Chairman of the Committee on Publication.
- 6. The Committee on the Library, to consist of the Librarian ex officio, and three other Fellows, one from each class, who shall examine the Library and make an annual report on its condition and management. This Committee, through the Librarian, shall report to the Council in March of each year, on the appropriations needed for the Library for the coming year. All bills incurred on account of the Library, within the limits of the appropriations made by the Academy, shall be approved by the Librarian.
- 7. The President and Recording Secretary shall be a Committee on the general expenditures of the Academy. This Committee shall report to the Council in March of each year on the appropriations needed for the general expenditures for the coming year, and either member of the Committee may approve bills incurred on this account within the limits of the appropriations made by the Academy.
- 8. An auditing Committee, to consist of two Fellows, for auditing the accounts of the Treasurer, with power to employ an expert and to approve his bill.
- 9. In the absence of the Chairman of any Committee, bills may be approved by a member of the Committee designated by the Chairman for the purpose.

## CHAPTER VI.

#### OF THE SECRETARIES.

1. The Corresponding Secretary shall conduct the correspondence of the Academy, recording or making an entry of all letters written in its name, and preserving on file all letters which are received; and at each meeting he shall present the letters which have been addressed to the Academy since the last meeting. Under the direction of the Council, he shall keep a list of the Resident Fellows, Associate Fellows, and Foreign Honorary Members, arranged in their Classes and in Sections in respect to the special sciences in which they are severally proficient; and he shall act as secretary to the Council.

- 2. The Recording Secretary shall have charge of the Charter and Statute-book, journals, and all literary papers belonging to the Academy. He shall record the proceedings of the Academy at its meetings; and after each meeting is duly opened, he shall read the record of the preceding meeting. He shall notify the meetings of the Academy, apprise officers and committees of their election or appointment, and inform the Treasurer of appropriations of money voted by the Academy. He shall post up in the Hall a list of the persons nominated for election into the Academy; and when any individual is chosen, he shall insert in the record the names of the Fellows by whom he was nominated.
- 3. The two Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the records of the meetings of the Academy as may seem to them calculated to promote its interests.
- 4. Every person taking any books, papers, or documents belonging to the Academy and in the custody of the Recording Secretary, shall give a receipt for the same to the Recording Secretary.

#### CHAPTER VII.

#### OF THE TREASURER.

- 1. The Treasurer shall give such security for the trust reposed in him as the Academy shall require.
- 2. He shall receive all moneys due or payable to the Academy and all bequests and donations made to the Academy. He shall pay all bills due by the Academy, when approved by the proper officers (except those of the Treasurer's office, which may be paid without such approval). He shall sign all leases of real estate in the name of the Academy. All transfers of stocks, bonds, and other securities belonging to the Academy shall be made by the Treasurer with the written consent of one member of the Committee of Finance. He shall keep an account of all receipts and expenditures, shall submit his accounts annually to the Auditing

Committee, and shall report the same at the expiration of his term of office or whenever called on so to do by the Academy or Council.

- 3. The Treasurer shall keep separate accounts of the income and appropriation of the Rumford Fund and of other special funds, and report the same annually.
- 4. The Treasurer may appoint an Assistant Treasurer to perform his duties, for whose acts, as such assistant, the Treasurer shall be responsible; or the Treasurer may employ any Trust Company, doing business in Boston, as agent to perform his duties, the compensation of such Assistant Treasurer or agent to be paid from the funds of the Academy.

## CHAPTER VIII.

#### OF THE LIBRARIAN AND LIBRARY.

- 1. It shall be the duty of the Librarian to take charge of the books, to keep a correct catalogue of them, to provide for the delivery of books from the Library, and to appoint such agents for these purposes as he may think necessary. He shall make an annual report on the condition of the Library.
- 2. The Librarian, in conjunction with the Committee on the Library, shall have authority to expend such sums as may be appropriated, either from the General, Rumford, or other special Funds of the Academy, for the purchase of books, periodicals, etc., and for defraying other necessary expenses connected with the Library.
- 3. To all books in the Library procured from the income of the Rumford Fund, or other special funds, the Librarian shall cause a stamp or label to be affixed, expressing the fact that they were so procured.
- 4. Every person who takes a book from the Library shall give a receipt for the same to the Librarian or his assistant.
- 5. Every book shall be returned in good order, regard being had to the necessary wear of the book with good usage. If any book shall be lost or injured, the person to whom it stands charged shall replace it by a new volume or set, if it belongs to a set, or pay the current price of the volume or set to the Librarian; and thereupon the remainder of the set, if the volume belonged to a set, shall be delivered to the person so paying for the same.
- 6. All books shall be returned to the Library for examination at least one week before the Annual Meeting.

7. The Librarian shall have custody of the Publications of the Academy. With the advice and consent of the President, he may effect exchanges with other associations.

#### CHAPTER IX.

#### Of Meetings.

1. There shall be annually four stated meetings of the Academy; namely, on the second Wednesday in May (the Annual Meeting), on the second Wednesday in October, on the second Wednesday in January, and on the second Wednesday in March. At these meetings, only, or at meetings adjourned from these and regularly notified, or at special meetings called for the purpose, shall appropriations of money be made, or alterations of the statutes or standing votes of the Academy be effected.

Special meetings shall be called by the Recording Secretary at the request of the President or of a Vice-President or of five Fellows. Notifications of the special meetings shall contain a statement of the purpose for which the meeting is called.

- 2. Fifteen Resident Fellows shall constitute a quorum for the transaction of business at a stated or special meeting. Seven Fellows shall be sufficient to constitute a meeting for scientific communications and discussions.
- 3. The Recording Secretary shall notify the meetings of the Academy to each Resident Fellow; and he may cause the meetings to be advertised, whenever he deems such further notice to be needful.

## CHAPTER X.

OF THE ELECTION OF FELLOWS AND HONORARY MEMBERS.

- 1. Elections shall be made by ballot, and only at stated meetings.
- 2. Candidates for election as Resident Fellows must be proposed by two Resident Fellows of the section to which the proposal is made, in a recommendation signed by them; and this recommendation shall be transmitted to the Corresponding Secretary, and by him referred to the Council. No person recommended shall be reported by the Council as a

candidate for election, unless he shall have received the approval of at least five members of the Council present at a meeting. All nominations thus approved shall be read to the Academy at any meeting, and shall then stand on the nomination list until the next stated meeting, and until the balloting. No person shall be elected a Resident Fellow, unless he shall have been resident in this Commonwealth one year next preceding his election. If any person elected a Resident Fellow shall neglect for one year to pay his admission fee, his election shall be void; and if any Resident Fellow shall neglect to pay his annual assessments for two years, provided that his attention shall have been called to this article, he shall be deemed to have abandoned his Fellowship; but it shall be in the power of the Treasurer, with the consent of the Council, to dispense (sub silentio) with the payment both of the admission fee and of the assessments, whenever in any special instance he shall think it advisable so to do.

- 3. The nomination and election of Associate Fellows shall take place in the manner prescribed in reference to Resident Fellows.
- 4. The nomination and election of Foreign Honorary Members shall take place in the manner prescribed for Resident Fellows, except that the nomination papers shall be signed by at least seven members of the Council before being presented to the Academy.
- 5. Three-fourths of the ballots cast must be affirmative, and the number of affirmative ballots must amount to eleven to effect an election of Fellows or Foreign Honorary Members.
- 6. If, in the opinion of a majority of the entire Council, any Fellow—Resident or Associate—shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his Fellowship; and provided that a majority of two-thirds of the Fellows at a stated meeting, consisting of not less than fifty Fellows, shall adopt this recommendation, his name shall be stricken off the roll of Fellows.

### CHAPTER XI.

#### OF AMENDMENTS OF THE STATUTES.

1. All proposed alterations of the Statutes, or additions to them, shall be referred to a committee, and, on their report at a subsequent stated meeting or a special meeting called for the purpose, shall require for

enactment a majority of two-thirds of the members present, and at least eighteen affirmative votes.

2. Standing votes may be passed, amended, or rescinded at a stated meeting, or a special meeting called for the purpose by a majority of two-thirds of the members present. They may be suspended by a unanimous vote.

### CHAPTER XII.

### OF LITERARY PERFORMANCES.

1. The Academy will not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its publications.

## STANDING VOTES.

- 1. Communications of which notice has been given to the Secretary shall take precedence of those not so notified.
- 2. Associate Fellows, Foreign Honorary Members, and Resident Fellows, who have paid all fees and dues chargeable to them, are entitled to receive one copy of each volume or article printed by the Academy on application to the Librarian personally or by written order within two years of the date of publication. Exceptions to this rule may be made in special cases by vote of the Academy.
- 3. The Committee of Publication shall fix from time to time the price at which the publications of the Academy may be sold. But members may be supplied at half this price with volumes which they are not entitled to receive free, and which are needed to complete their sets.
- 4. Two hundred extra copies of each paper accepted for publication in the Memoirs or Proceedings of the Academy shall be placed at the disposal of the author, free of charge.
- 5. Resident Fellows may borrow and have out from the Library six volumes at any one time, and may retain the same for three months, and no longer.
- 6. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.
- 7. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy, except by special leave of the Librarian.
- 8. Books, publications, or apparatus shall be procured from the income of the Rumford Fund only on the certificate of the Rumford Committee that they, in their opinion, will best facilitate and encourage the making of discoveries and improvements which may merit the Rumford Premium; and the approval of a bill incurred for such purposes by the Chairman shall be accepted by the Treasurer as proof that such certificate has been given.
- 9. A meeting for receiving and discussing scientific communications may be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September.

## RUMFORD PREMIUM.

Iu conformity with the terms of the gift of Benjamin, Count Rumford, granting a certain fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of said fund, as it now exists, at any Annual Meeting, an award of a gold and a silver medal, being together of the intrinsic value of three hundred dollars, as a premium to the author of any important discovery or useful improvement in light or in heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands; preference being always given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind; and to add to such medals, as a further premium for such discovery and improvement, if the Academy see fit so to do, a sum of money not exceeding three hundred dollars.

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