

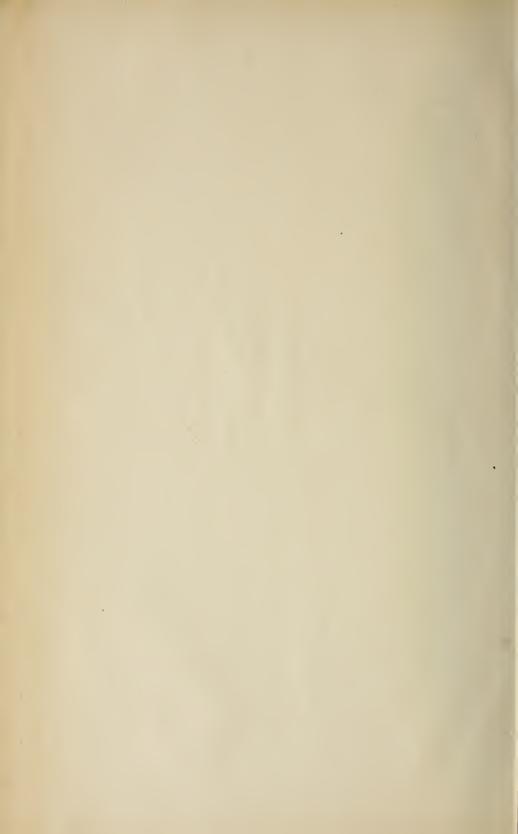




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#### THE

36

# AMERICAN JOURNAL OF SCIENCE.

#### EDITORS

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the issuance of the lists of many things collected and received during the past year.

#### BOOKS, NEW ARRIVALS.

I have recently purchased a large number of books from the libraries of I. C. Martindale, the well known botanist; G. W. Carpenter, for many years treasurer of the Academy of Natural Sciences of Philadelphia, and others. They include such rare books as the following.

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THE

### AMERICAN JOURNAL OF SCIENCE

#### [THIRD SERIES.]

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ART. I.—Studies of the phenomena of Simultaneous Contrast-Color; and on a Photometer for measuring the intensities of Lights of different Colors; by ALFRED M. MAYER.

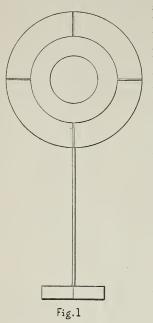
It is often desirable in the study of simultaneous contrastcolors to have large surfaces colored by contrast, so that we can the better match the colors of these surfaces with rotating colored disks and thus arrive at quantitative statements of their hues. This is especially desirable in ascertaining the hues of the light of flames, of the Welsbach incandescent lamp and of the arc electric light when compared with day light, or, when compared one with another. The result of many experiments is the apparatus described in the following section and which is useful for this purpose.

Screen for ascertaining the hues of lights and the contrastcolors of these lights.—A ring is formed of white card-board by cutting out a central opening of  $12^{\text{cms}}$  in diameter in a disk of  $22^{\text{cms}}$  in diameter. This ring has a breadth of  $5^{\text{cms}}$ . Another ring is made similar to this one, except that it has four narrow radial arms to support a disk of thin translucent white paper,\*  $35^{\text{cms}}$  in diameter. This paper disk is placed between the rings, which are then fastened together and screwed to a thin rod, on a stand, as shown in fig. 1.

\*Trials with many kinds of paper showed that a white linen tracing-paper was the best. It is not possible to describe this so that one may be sure of selecting a similar paper. It was obtained of Keuffel and Esser, Fulton St., N. Y., and sold as "No. 202 Alba tracing paper."

AM. JOUR. SCI .- THIRD SERIES, VOL. XLVI, NO. 271.-JULY, 1893.

Place the screen, thus formed, in front of a petroleum lamp and exclude the daylight from the side thus illuminated. The other side of the screen is illuminated by the light of the sky



admitted through a distant window. The cardboard ring is thus illuminated on one side only by the lamp; on the other side, only by the daylight. The translucent paper transmits the lamplight to the side facing the window, while it transmits the daylight to the side facing the lamp. On the side of the screen facing the window the cardboard ring appears cyan-blue while on the side facing the lamp the ring appears orange yellow.

*Hues of the sides of the ring.*—An idea of the hues and intensities of these colors, which cause astonishment even in those who are experimenters in chromatics, will be given by the description of the following experiments.

By means of a Bunsen-photometer disk I adjusted the distance of the lamp from the screen so that I obtained, as nearly as I could judge, equal illumination of the sides of the

screen. I then found that the blue was matched in a rotator by a disk having a sector of 60 parts of the circumference of Prussian blue, with a sector of 10 parts of emerald-green and a sector of 30 parts of white cardboard. The blue was that of one of the many colored disks given me by Professor O. N. Rood and was marked, "Blue between cyan-blue and the ultramarine of the physicist, but nearer the latter. Near F and on its more refrangible side. Made with Prussian blue." The blue on this disk appeared as saturated in hue as could be made by the pigment.

The match of the color of the side of the ring facing the lamp, L in fig. 3, was obtained by placing a silvered mirror, M, so that the reflection of this side of the ring, S, was seen close to the rotator, R.

The color of the cardboard ring facing the lamp was matched by the rotation of a disk formed of 50 parts of chrome yellow, 30 parts of red lead (red orange) and 20 parts of white cardboard. Such appears to be the hue of the light of a petroleum flame when compared, in this manner, with the light of the sun.

The petroleum flame used in these experiments was that of a Belgian burner, giving about 35 candles. The daylight was obtained from a window 85<sup>cms</sup> square; the lower half of which when viewed from the screen, was occupied by the snow-clad surface of an opposite hill. The day was very clear, and the sky very slightly tinted with blue.

The colors of the sides of the ring of the screen are complementary. - I combined the Prussian blue, emerald green, chrome yellow and orange red on a disk on the rotator and found that when the disk was formed of sectors having 60 parts of Prussian blue, 11 of emerald green, 19 of chrome yellow, and 10 of red lead, I obtained a gray which was exactly matched by a central disk formed of 71 parts of dead ivory-Fig. 3. black and 29 of white cardboard. See fig. 2. These measures gave the following equation:

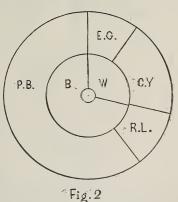
 $\left\{ \begin{array}{l} 60 \quad \mbox{Prussian blue} \\ 11 \quad \mbox{Emerald green} \end{array} \right\} + \left\{ \begin{array}{l} 19 \quad \mbox{Chrome yellow} \\ 10 \quad \mbox{Red lead} \end{array} \right\} = \mbox{Gray} \left\{ \begin{array}{l} 71 \quad \mbox{Black} \\ 29 \quad \mbox{White} \end{array} \right\}$ 

It is rather difficult to get the exact match on the rotating disk of the hues on the front and back of the card-board ring

of the screen on account of the illumination of these surfaces. The rotator must be placed nearer the window than the screen so that it is well illuminated.

The equation shows that the cyan-blue of 60 parts of Prussian blue + 11 of emerald green is complementary to an orange yellow of 19 of chrome yellow The hue of +10 of red lead. this orange of the lamp side of the ring, as given by the rotator was 50 chrome yellow + 30 red lead + 20 white, which mixture

- R



is approximately in the proportion of 19 to 10. The correspondence of the two experiments is, I suppose, about as near as could be expected from the difficulty of matching the illuminated hues of the ring of the screen.

The small central disk on the rotator gave a gray of 71 parts of ivory-black + 29 of white cardboard, which matched the gray given by 71 parts of cyan-blue +29 parts of orange.

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4 Mayer—Phenomena of Simultaneous Contrast-Color,

Calling the intensity of the orange 100, we have  $100 \times 29 = 71$  I, which gives for I (the intensity of the cyan-blue), only 40.8 per cent of that of the orange.

The orange yellow of the side of the ring facing the lamp and of the side of the translucent paper facing the daylight is complementary to the cyan-blue of the side of the ring facing the daylight and of the side of the translucent paper facing the lamp.

In fig. 4, L is the lamp; S, the screen which in this experiment is deprived of the border of translucent paper; W, the window; M, a silvered mirror which reflects the back of the screen to the eye which looks through an achromatized double refracting calc spar prism at C.S., and sees two images of the side of the screen reflected from the mirror and two images of the side of the screen facing the window. By suitably inclining and rotating the calc spar prism these images may be brought into the positions shown in fig. 5, in

which A represents one of the images of the side of the screen facing the window; B, the other image of the same; C, is one of the images of the side of the screen facing the lamp and seen by reflection from the mirror.

> The overlapping of these images, when the illumination is properly adjusted, gives the following results, as shown by the letters in fig. 5, where B stands for cyanblue, Y for orange yellow, and W for white. The translucent paper Y of B overlaps the ring

of A and gives white, and the blue of the ring of B overlaps Y of the translucent paper of A and gives white. In the same manner the orange yellow of the cardboard ring of C overlaps the blue of the ring of A and gives white. Where the ring of C overlaps the translucent paper of A there is a more intense orange, and when the blue of the translucent paper of C overlaps the blue of the ring of A we have a more intense blue. On bringing B of the translucent paper of C over Y of the translucent paper of A we have white.

Experiments on the complementary colors of gratings.—Out of thin cardboard, such as is used for thin visiting cards, I cut

Ø\_C.S.

M ...

Fig.4.

W

C Fig. 5.

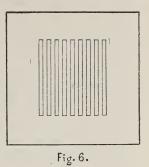
gratings with a dividing engine. See fig. 6. The widths of the spaces cut out of these gratings exactly equalled the breadths of the cardboard left in the grating. Gratings were thus made having spaces of 1, 2, 3, 4 and 5<sup>mm</sup>. The cardboard is rendered opaque by coating one side of it with ivory-black in dilute shellac varnish. After it has dried the cardboard is well flattened before it is fastened to the surface of a piece of hard wood on the dividing-engine. The cutting edge of the cutter for this work must have a very acute

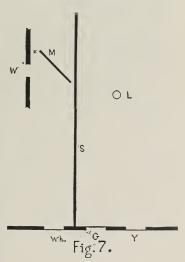
angle. I made one by grinding down a rod of Stubs' steel. Heating this to a dull cherry red and then forcing it into a large ball of beeswax gives the edge of the cutter the required temper, without the necessity of subsequently "letting it down." The

blackened side of the gratings was covered with the "Alba tracing paper." The grating was mounted back of an opening in a black cardboard screen, so that only the white grating was exposed. Two other black screens, Wh and Y of fig. 7, having openings of the same size as the grating and covered on the back with the translucent paper, were placed on either side of the grating, G. In fig. 7, L is the lamp. The window is on the other side of G. The screen S divides the apparatus so that the light of the window W reflected by the mirror M on to the screen Wh cannot fall on G or on Y, which are only illuminated by the lamp L.

The translucent paper of the grating G and of the screen Y appear orange yellow. The bands of white cardboard of the grating appear cyan-blue. The translucent paper of the screen Wh is white.

Sit a little to one side of the grating so as not to intercept the light from the window, and look at the grating through the calc-spar prism. Rotate it till the blue bands of the grating are superposed on the orange bands, when, if the surface of



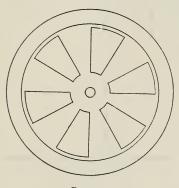


the grating is equally spaced, the superposed surfaces appear white when compared with the white of the screen Wh. Without the screen Wh the eye has no term of comparison and may take a yellowish white for white. The illumination of the screen Wh should be made equal that of the superposed images of the grating.

When this experiment is carefully made, with the proper illumination, the effect is surprising when, in favorable conditions, on rotating the prism you see the grating actually obliterated with no bands visible, but only a uniform white surface. The grating with spaces of 3<sup>mm</sup> gave the best results:

In experiments with the screen, fig. 1, formed of the cardboard ring and the translucent disk, it is easy, by altering the relative intensities of the daylight and lamplight and by changing the distance of the lamp from the screen, to produce great changes in the saturation of the contrast-colors. Indeed I have sometimes thus obtained, towards nightfall, a cyan-blue so saturated in hue that little or no white was required in the disk of the rotator to match the color on the ring. In the same manner similar changes in color have been observed in the hue of the ring illuminated by the lamp.

On illuminating one side of the screen by daylight and the other by the white light of a Welsbach incandescent lamp, and



#### Fig. 8.

then placing colored glasses or films of colored gelatine between the screen and the Welsbach lamp effects of contrast are obtained which are so readily imagined by the physicist as to require no description; but they are worth viewing.

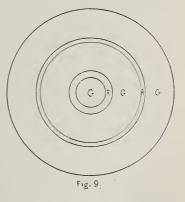
Increase of the purity and luminosity of the contrast colors by a rotating screen.—Make a disk of white cardboard of 27<sup>cms</sup> in diameter, with eight sectors cut out of it, and cover it with translucent paper so that the paper extends beyond the disk

and makes a border  $3^{\text{cms}}$  wide. A circle of  $8^{\text{cms}}$  in diameter is left in the center of the disk and a ring of  $1\frac{1}{2}^{\text{cm}}$  on its border. This disk is shown in fig. 8, but with only six sectors. It should have eight. It is placed between the lamp and the window, and rotated with a velocity of one revolution in about  $1\frac{1}{4}$  seconds, while it is viewed on the side facing the window. The blue sectors thus take successively the places just before occupied by the sectors of orange-yellow and the effect is to heighten the contrast-color in such a remarkable manner that the blue sectors by their more intense color appear separated from the rim and central circle appear in a plane farther from the eye than the plane of the center and rim. On the side of the disk illuminated by the lamp the same effects are produced, only they appear more marked. A change will also be observed in the hue of the advancing and following edges of the sectors, on both sides of the disk ; the advancing edges appearing more saturated in hue than the following edges.

A mode of observation by which contrast-colors are intensified.—Simultaneous contrast-colors are generally viewed by placing gray or tinted surfaces on colored grounds, or by the juxtaposition of colored surfaces. The effects thus produced are of such constant occurrence in the paintings of artists, and in colored fabrics, that their study is of great interest. The contrast-colors thus produced have generally been studied by simply placing on a colored ground smaller gray or tinted surfaces and observing these with the unaided eye. This method has been improved by H. Meyer\* who viewed the gray on the colored ground when both were covered with white transparent paper.

The mode of observation I have devised for the study of contrast-colors is as follows. A glass tube of  $2.7^{\text{cms}}$  in interior diameter and  $10^{\text{cms}}$  long is coated on the outside with black Japan varnish, so as to have reflection only from the interior surface of the tube. A ring of  $3^{\text{cms}}$  in diameter with a central opening of  $2^{\text{cms}}$  is cut out of gray paper. The gray of this ring was matched on the rotator

by a disk having 57 parts of ivory-black and 43 parts of white Bristol board. This ring, placed on a surface of emerald green appears of a rose color. If at the distance of distinct vision we look at the ring through the tube we shall see the ring by direct vision inclosing a circle of green and surrounded by a ring of emerald green, and this inclosed by a rose colored ring, produced by reflection from the interior of the tube, and sur-



rounding this ring is another of emerald green, as shown in fig. 9; in which R and R are the red rings and G, G, and G, the circle and the two rings of emerald green.

\* Pogg. Ann., xcv, 170.

The hue of the rose-colored rings as seen through the tube is much more intense than the hue of the ring viewed on the emerald ground with the unassisted eye. Experiments made with the aid of an achromatized calc spar prism, and by matching on a rotating disk the colors of the gray ring on an emerald green ground showed that the intensity of the contrast-color, as seen with the reflecting tube is nearly double of what it is when viewed by the eye alone. The color of the ring when viewed by the unassisted eye was matched on the rotator by a disk having 30 parts of Chinese vermillion + 7 of "Hoffman's violet R. R. R." + 34 parts of ivory black + 29 of white Bristol board. As seen through the reflecting tube the match appeared to be given by 57 of Chinese vermillion + 15 of "Hoffman's violet R. R. R." + 28 of white Bristol board.

Another tube, 4.5<sup>cms</sup> in diameter and 18<sup>cms</sup> long gave excellent results, with two reflected rings, and on nearer vision, with four reflected rings. A tube, suitable for these experiments, is selected by closing one of its ends by a disk of cardboard having a pin hole at its center. When the end with the pin hole faces the sky and we look through the other end we see bright rings caused by the reflection of the light of the pin hole from the surface of the tube. If these rings are circular and concentric the tube is of circular section and its axis is a right line.

The value of this mode of observation is shown by the following experiments. Place the ring of gray paper, or, a circle of gray paper, about  $1\frac{1}{2}^{cms}$  in diameter, on a surface painted with cobalt blue, not too saturated. The gray ring, or, circle, appears of an orange tint. Place a similar gray ring, or, circle, on a surface lightly washed with emerald green, it appears pinkish. The difference between the hues of the ring when viewed on the cobalt blue and on the emerald green though decided is not strongly marked; but if viewed through the reflecting tube the ring on the cobalt blue appears of a rather intense orange and the ring on the emerald green appears of a rose color. When so viewed the difference in these hues is strongly marked.

Pieces of card-board, painted with the following colors, were arranged in pairs. Orange yellow on the less refrangible side of D, and orange yellow on the more refrangible side of D. Greenish yellow and yellowish green, both made with gamboge and Prussian blue. Purple of violet end of spectrum with added red, made with Hoffman's violet R. R. R., and violet between G and H, Young and Müller's fundamental color. Place a pair of the colors, as given above, side by side and on each put a gray ring, with a reflecting tube over each ring. When viewed by the unassisted eye the differences in

hue are slight and difficult to define; but when viewed in rapid succession through the adjoining tubes the differences in hue are decided and may be readily matched in color with disks on the rotator.

The duration of the time of vision necessary to perceive contrastcolor.—A square screen was made, as shown in fig. 10, with a square of cardboard in its center,  $8^{cms}$  on the side, surrounded by a square of translucent white paper,  $35^{cms}$  on the side. This screen was placed between the petroleum flame and the window so that its sides were

the window so that its sides were equally illuminated. On the side facing the window the central square appeared cyanblue. One-half of this square was covered by a strip of paper so tinted with orange yellow that it appeared gray when in juxtaposition with the other blue half of the square.

On a rotator was placed two superposed black disks of the same diameter  $(25^{\text{cms}})$ . Near the periphery of each disk was cut out an annular slot,  $4^{\text{cms}}$ long and  $6^{\text{mm}}$  wide, as shown in fig. 11. By turning one of these disks on the other the opening of this slot could be varied from  $4^{\text{cms}}$  to nothing. The rotator is so made that the time of a rotation of the disk can be held uniform and also accurately measured. On gradually narrowing the opening in the slit the dura-

tion of vision of the blue and gray square was reduced to  $\frac{1}{1600}$  of a second, when the blue half of the square could not be distinguished from the gray half.

When the screen was illuminated by a more orange light, obtained by placing a sheet of orange gelatine between the lamp and the screen, the gray and blue were not distinguishable when the duration of vision was  $\frac{1}{1300}$  of a second.

In these experiments I only got 11.6 flashes of light from the screen in a second, while the number of flashes required to banish all flickering from the screen was accurately measured as  $\frac{1}{46}$  of a second with the illumination of the lamp alone, and  $\frac{1}{42}$  of a second when the lamp-light traversed the orange gelatine film. These experiments show, what is well known, viz: that as the intensity of the light diminishes the duration

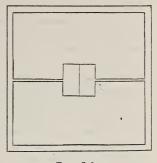


Fig.10.



of no perceptible change in the intensity of the residual impression increases. I found that the light from a white cloud, seen, near noon, through a north window on a clear day lasts only  $\frac{1}{68}$  of a second before the residual effect diminishes.

A gray ring was placed on an emerald green ground facing the light from a bright white cloud. When viewed through the opening in the rotator the ring appeared pink on the green ground till the duration of the vision of the ring was reduced to  $\frac{1}{8380}$  of a second, when the ring ceased to be visible on the emerald green ground; but so long as it was visible the contrast color was visible. I found that 43 flashes per second were necessary to render the vision of the pink ring and green ground steady, without the least flickering, while only 11.6 flashes per second were obtained in determining the  $\frac{1}{8380}$  of a second as the time when contrast-color ceased to be visible. The fact that the contrast color of the ring remained till the ring could not be distinguished from the green ground gave the opinion that I ceased to obtain contrast-color because the narrow slit used gave too little light to the eye. On doubling the width of the slit and doubling the velocity of rotation the contrast-color of the ring reappeared, though the duration of vision was the same as in the former experiment.

Experiments on simultaneous contrast-colors produced by the flash of the electric discharge.—The foregoing experiments having proved insufficient to form any opinion as to the time of vision necessary to perceive simultaneous contrast-color I made the following experiments with the light obtained by the discharge of a Holtz induction machine.

The gray ring was placed on the emerald green ground near a Holtz machine, which gave a very bright flash of 8<sup>cms</sup> long. The condensing surface on the two jars connected with the electrodes of this machine equalled 135 square centimeters. Professor O. N. Rood\* measured the duration of the flash of Leyden jars of 738 and 71 square centimeters of surface, charged by an inductorium. The durations of the discharges of these jars were respectively  $\frac{1}{5,700,000}$  second and  $\frac{1}{25,000,000}$ of a second. From these measures I infer that the duration of the flash of the Holtz machine did not exceed the 10,000,000 of a second. With short striking distances between the electrodes the flash is formed of several separated acts, as shown by Henry, + Feddersen, ‡ Rood, § and Mayer. In the case of the discharge of a large inductorium the writer ( $\parallel$ ) has shown that when the striking distance between brass ball electrodes is only one millimeter, with a Leyden jar of 242<sup>sq cms</sup> of sur-

\* This Journal, Sept., 1871

† Pogg. Ann.. vol. cxvi, p. 132. This Journal, Dec., 1874. + Proc. Amer. Phil. Soc, 1842. § This Journal, Oct., 1872. face in the circuit, the discharge lasts  $\frac{1}{24}$ th of a second and is formed of over 120 separate sparks; but as the striking distance is increased the discharge is formed of fewer and fewer components, till at a striking distance between 1 and 2<sup>ems</sup> the discharge is reduced to a single flash. In the following experiments the striking distance is 8<sup>ems</sup>, and a single flash was given, whose duration we may safely assume was less than  $\frac{1}{1.000,000}$  of a second.

In a dark room, at night, the flash of this machine gave vivid contrast-colors. The gray ring appearing bright pink on an emerald green ground, and of a bright yellow on an ultramarine ground. The after images of these effects lasted about  $\frac{1}{2}$  of a second.

A rod was placed in front of a white cardboard and the shadow of the rod was formed on the screen by a candle. The distance of the candle was such that the white cardboard appeared equally brilliant when illuminated only by the candle, or, only by the electric flash. At the moment of the flash the appearance presented was very remarkable. From the shadow of the candle appeared suddenly to shoot a dark screen, which had superposed the shadow of the candle, and which shot to the side of the shadow and appeared of a bright golden orange, while the apparently uncovered shadow of the candle appeared

of a brilliant cobalt blue; to my eye exactly as though an opaque screen had been suddenly removed from a slit in the shutter of a d ark ened room, which slit was cov-

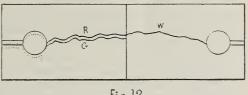


Fig.12.

ered by a piece of cobalt glass.

A square of thin green glass,  $4^{\rm cms}$  by  $6^{\rm cms}$ , was placed on a piece of thin silvered glass,  $4^{\rm cms}$  by  $12^{\rm cms}$ , so that the edges of the green glass and of the silvered glass coincided. This arrangement gave a surface, half of silvered mirror, half of green glass. This apparatus was so placed that the electrodes of the machine and the flash were reflected from it to the eye. The room was dark. At the moment of the flash its reflection appeared as in fig. 12. On the mirror the line of the discharge was white; W in the figure. The continuation of this line on the surface of the green glass appeared red (R in figure), though really white. In front of and parallel to this line was a green line, G, produced by the light of the flash reflected from the surface of the silvered mirror, and having traversed

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#### 12 Mayer—Phenomena of Simultaneous Contrast-Color,

twice the thickness of the green glass. In this experiment we obtain contrast-colors in the source of light itself.

The explanation of the phenomena of simultaneous contrastcolors, as generally given in works on chromatics, is that they are due to "error of judgment," to "deception of judgment," or to "fluctuation of judgment." The reasoning given may be convincing if all the conditions really exist which the writers assume to exist in their explanations of these phenomena. One of these conditions is that a judgment can be formed in the minute interval of time only necessary in which to perceive contrast-colors. In the experiments just described with the electric flash we have *apparently* instantaneous perception of the contrast-colors in the gray ring placed on the green and ultramarine grounds, in the candle and electric light shadows and even in the very flash itself when this is seen reflected from the top surface of a green glass and from the mirror on which the green glass rests.

Many careful experiments made by me and others, using as chronometer three pairs of forks of the octave of UT<sub>6</sub>, giving respectively 10, 12 and 15 beats per second, showed that certainly the interval between the flash and the perception of the colors was much less than  $\frac{1}{15}$  of a second. Indeed, on viewing the flash and the illuminated surfaces at the same time, or, hearing the discharge and viewing only the illuminated ring, no interval could be detected by this mode of observation as existing between the instant of the flash and the perception of the colors, and we certainly could have detected a shorter interval than  $\frac{1}{15}$  of a second had it existed.

Incidentally, I will here state that when different geometrical or irregular figures cut out of white paper and placed on an ivory-black ground were illuminated by the electric flash, the observer, so far as I could ascertain formed conclusions as to the forms of the pieces of paper in an interval of time less than the  $\frac{1}{10}$  of a second. Certainly the interval of time required to reach a conclusion as to the contrast-color was less than the  $\frac{1}{15}$  of a second. Professor Mendenhall in 1871 (this Journal) gives 0.292 sec. for the time required by an observer to respond, by means of an electric chronograph, to the appearance of a white card. When the observer responds by touching the circuit key with one hand when a white card appears, and with the other hand when a red card appears, Professor Mendenhall finds 0.443 sec. as the time required for the response. Subtracting the first number from the last he obtains 151, or  $\frac{1}{6}$  sec., as the time to form a judgment between white and red. Similar experiments gave him 0.202, or  $\frac{1}{5}$  sec., as the time to judge whether a circle or a triangle appeared to the observer. The intervention of the

operation of brain, nerve and muscle before the response is recorded involves complex operations, and the action of right or left sides of brain when the two hands are used. It appears that the plan of eliminating these actions and thus obtaining a residual time which is attributed to the interval required to form a judgment of color or of form is faulty. I am sure that if estimation of the time required for such mental operations is made by the *continuous indications* of the beats of forks, such intervals as  $\frac{1}{6}$  and  $\frac{1}{5}$  of a second will at once appear much in excess of the time respectively required to form a conclusion as to whether a white or red color or a circle or triangle has been presented to our vision.

It is here to be noted that although the after-images in these experiments with the electric flash lasted about  $\frac{1}{2}$  of a second, vet the most careful scrutiny could detect no change in sensation at and immediately following the flash. The contrast. colors, so far as I and others observed, appeared at the moment of the flash. After the instant the image of the flash is formed on the retina there exists, no doubt, an interval of time before we are conscious of the stimulus, whose effects are seen rapidly to rise and then more gradually to fall, falling with two oscillations in intensity, so that all the events of the phenomenon take place in about  $\frac{1}{2}$  of a second. However, no vague impression of surfaces merely differing in illumination and then suddenly changing into a color and its contrast-color could be detected. I think that this interval of no color sensation, if it exist, must be of exceedingly short duration; but such a period of light without color cannot be detected, and if it cannot be perceived, then, so far as we are concerned, it appears to me, that there can be no hesitation in the perception of the colors, and no "fluctuation of the judgment" and "dividing between two images the difference in color which really exists" before the mind reaches its conclusion as to the character of the colors.

The following experiments were separately made on three persons between whom no communication had passed as to the nature of the experiments to be tried on them. I placed a gray ring on a ultramarine disk in front of the Holtz-machine and requested the observer, who had implicit confidence in my truthfulness, to describe to me as accurately as possible the exact hue of the pink, or rose color, or red he would see on a green ground at the instant of the electric flash. Each observer at once said: "it is not pink, the ring appears yellow on a blue ground." Now in each of these experiments the observer was prepared, by my pardonable lying, to see red on a green ground, and to see yellow on a blue ground his mental condition of anticipation to see red on a green ground was first removed then a new departure was taken and a judgment formed which resulted in his seeing yellow on a blue ground, and all that in a minute interval of time.

I do not know if psychologists have come to a conclusion as to the smallest interval of time necessary to form a judgment, either true or false, or in which to have a "fluctuation of the judgment," or in which "to exercise judgment and divide between two colors the difference in colors which really exist." If such mental operations can be performed in the millionth, the thousandth, or even in a few hundredths of a second then the explanations of these phenomena, as generally given, may be convincing.

Von Bezold in his "Theory of Color," Boston, 1876, in explaining the fact that a rod seen by reflection from a piece of green glass laid on a mirror gives two images one green the other red, says: "As the observer does not *know* which of the two images is the colored one he exercises his judgment, and divides between the two images the difference in color which really exists." Now this experiment is similar in its conditions and in its effects of contrast-color to the one I made on the contrast-colors of the electric flash, when the same colors were distinctly seen apparently at the moment of the discharge. Can one "exercise his judgment and divide between the two images the differences in color which really exists" in an interval of time which is less than  $\frac{1}{15}$  of a second?

In the experiment of the colored shadows cast by the candle and by daylight, these colors are explained by Von Bezold (pp. 152, 153), as follows: "The spot occupied by the blue shadow is illuminated by the white daylight, the larger white surface by daylight and by candle light, the other shadow by candle light only. It might be presumed, therefore, that one of the shadows would appear white the other yellow. This is not the case, however; for *knowing* the surface to be white we still take it to be white after it has really received the yellow light of the candle. Our judgment is led astray regarding white, and hence we believe the place occupied by the second shadow to be blue, although it is actually white." Helmholtz ("Lectures," N. Y., 1873, p. 267), says : "Thus in the experiment described above of colored shadows thrown by day-light and candle light the doubly illuminated surface of the paper being the brightest object seen gives a false criterion for white. Compared with it, the really white but less bright shadow thrown by the candle looks blue." These explanations assume knowledge and conditions which are not essential. If this knowledge and these conditions were necessary to see the phenomena then these explanations of the phenomena might be convincing; but the conditions they assume are not necessary. The following experiments show that there is no necessity at all in "knowing the surface to be white" or to see "the doubly illuminated surface of the paper."

The experiment of the colored shadows cast by the candle and by daylight was arranged behind a screen, so that no one could divine what was there. A tube blackened on the inside went obliquely through the side of the screen and was so adjusted that the circular field of view through the tube was entirely filled by equal portions of the two shadows, which formed two semicircles, one colored orange the other blue. The two persons on whom I experimented were ignorant of the phenomena of contrast-color and moreover were misled as to what they would see on looking into the tube, and I was specially careful not to speak to them about color. These persons were strangers to each other and neither knew that the other had been the subject of my experimenting. The first observer at once reported : "I see a circle half yellow and half blue." The other said: "I see a golden band next to a skyblue band and the golden band is rather deeper in color where it is next to the blue," which is certainly a very good description.

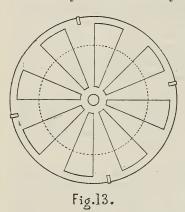
Having in mind the facts established by the foregoing experiments it seems to me that we have either to regard the phenomena of simultaneous-contrast color as psychical phenomena of which no satisfactory explanation has been given, or, we must discard the Young-Helmholtz hypothesis of color sensation and adopt one similar to that of Hering, which gives a direct physiological explanation of contrast-color effects without the psychological considerations which those who adopt the Young-Helmholtz hypothesis are obliged to resort to in their explanation of these phenomena; and which explanations, as I have attempted to show, are faulty, and have to be modified to be convincing.

According to Hering's hypothesis of color sensations when a portion of the retina is stimulated, adjoining portions of the field of view are affected by a sort of inductive action; so that changes are produced which are antagonistic or complementary to those portions of the retina actually stimulated.

M. Foster in his "Physiology, Lond., 1891," Part IV, bk. III, gives an excellent discussion of the relative merits of the Young-Helmholtz hypothesis and Hering's in explaining color sensations. In conclusion he writes . . "so far as we are aware no crucial test between the two has as yet been brought forward. We may now leave the matter with the remark that while the Young-Helmholtz theory tends to lead us direct from the retinal image to the psychological questioning of the sensations, and seems to offer no bridge between the first step and the last, Hering's theory is distinctly a physiological theory, and at least holds out for us the promise of being able to push the physiological explanation nearer and nearer home before we are obliged to take refuge in the methods of psychology."

A Photometer for measuring the intensities of differently colored lights.—It has already been shown that, in certain conditions of illumination and in certain directions of sight, a screen formed of perforated cardboard covered with translucent paper appears with complementary colors, and that if the screen be in the form of a disk with alternate sectors cut out of it, and is illuminated on one side by daylight and on the other side by lamplight, that the blue of one side of the disk and the orange of the other appear intensified on slowly rotating the disk. On increasing the velocity of rotation the complementary colors gradually blend and when the velocity of rotation has banished all flickering light from the disk it The side facing the daylight has a appears nearly white. slight yellowish tint; the side facing the lamp appears whiter, but is tinted with a feeble bluish hue.

To study more minutely these phenomena I made a disk



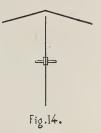
which could be readily taken apart and mounted with different translucent papers and have attached to it disks and rings of various colors. I shall call this disk, *the photometer disk*. It is made as follows:

Two disks, 13<sup>cms</sup> in diameter, and having eight sectors cut out, as shown in fig. 13, was made of thin Bristol board. A circle of 2<sup>cms</sup> in diameter was left in the center of the disk, from which the cardboard sectors radiate. The border of the disk is a ring of  $\frac{1}{2}$ <sup>cm</sup> wide, which was painted

black. Clamps, made of thin hammered brass, held these disks together.

Between these disks was placed a circle of the same white translucent paper used in the construction of the large contrast-color screen, fig. 1, and the disks were clamped together with the open sectors of the two disks coinciding in position. A black disk of  $8 \cdot 2^{\text{cms}}$  in diameter was placed on each side of the photometer disk, thus leaving between it and the black peripheral ring an annular space of  $1 \cdot 9^{\text{cm}}$  wide, formed of alternate spaces of cardboard and of translucent paper. The disk was mounted on a rotator and placed opposite two silvered mirrors inclined at an angle of  $150^\circ$ ; an arrangement similar to that of Letheby for observing the disk of Bunsen's photometer. The plane of the disk of the rotator bisected the angle formed by the mirrors, as shown in

fig. 14, so that the surfaces of both sides of the disk could be seen simultaneously, or, rather, in rapid succession. On rotating the disk while illuminated by daylight on one side and by lamplight on the other, the side illuminated by daylight appeared white tinted with yellow; the side facing the lamp appeared white tinted with blue. The hues were the same as described in the experiment with the large disk, fig. 8, only the surfaces



appeared brighter by contrast with the black center and border.

The feeble character of the hues on the photometer disk led me to hope that I could bring these to the same hue on both sides of the disk by the effects of contrast. To accomplish this I placed on the daylight side of the photometerdisk a compound disk formed of three split disks, one of red lead, one of chrome yellow, the other of white Bristol board. On the lamplight side I placed a disk formed of three split disks, colored ultramarine, emerald green, and one of white Bristol board. On rotation, the compound disk on the daylight side gave an orange yellow; on the lamplight side the disk gave a bluish green. These colors corresponded in hue to those seen on the respective sides of the ring of the photometer disk when it is rotated, only the hues were much more saturated. After a few trials I brought, by the contrast effects of these colored disks, the tints on the two sides of the ring of the photometer to the same hue; the translucent ring appearing white with a very slight orange yellow tint on both of its sides. The greenish blue had by contrast effect obliterated the blue tint of the ring and even replaced it by a very feeble orange yellow; while on the other side of the ring the orange yellow disk had diminished the orange yellow tint of the ring to the same feeble orange yellow as seen on the other side of the ring.

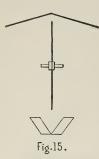
Experiments were now made to test this apparatus as a photometer. Equality of illumination cannot be determined with any precision if the two surfaces compared differ even slightly in hue. Here we had the same hue to deal with on both sides of the ring; which condition is different from the Bunsen photometer on which we have two colors on each side

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of the disk. Various methods were tried to render reliable the comparison of the illumination of the two sides.

(1) I used the eye alone, regarding only the portions of the ring on the border near the mirror, as shown in fig. 14.



(2) Two prisms reflected the images of portions of the sides of the ring nearest the mirror to juxtaposition, as shown in fig. 15.

(3) A tube blackened on the inside, with a black screen on the end next the disk, as shown in fig. 16, was used. The eye was thus shielded from extraneous light and the comparisons of illuminations was made, as in experiments 1 and 2, on the portions of the rings which were nearest the mirror as shown in fig. 16. Vision through this screened tube gave the best results.

After practice in such comparisons, made during several hours on different days, I became more and more skillful and the results of measurements become more concordant; but



Fig. 16.

such methods of photometry do not approach the accuracy of those in which two contiguous surfaces of different degrees of translucency coalesce into one surface of a uniform illumination, as happens on the balance of illuminations on the two sides of a Bunsen photometer disk when these are illuminated by lights of the same intensity and of exactly the same hue. A photometer for this mode of observation is described in the following section. It has, however, the advantage over the Bunsen photometer in that

it serves to measure the intensities of differently colored lights.

The Rotating-Disk Photometer.—The photometer disk was taken apart and a ring of thin white linen paper\* of the diameter of the disk and  $\frac{9}{10}$ <sup>cm</sup> wide was laid on one of the disks; this was covered by the circle of thin translucent white paper and on this was laid another ring of the thin linen paper. The disks were now clamped together. The outer portions of the open sectors of the disk were thus closed by two thicknesses of the thin linen paper with the "alba tracing paper" between them, a, in fig. 17; while the inner portions of the sectors were closed by the tracing-paper alone, b, in fig. 17.

On rotating the disk, it was not possible to balance the colors of the outer half (a in fig. 17), of the ring formed of

\*The best paper I have experimented with for this purpose is water-marked "Crane & Co., Dalton, Mass., Bond, No. 21."

three thicknesses of paper, with the same central colored disks, used in the previous experiment. when one side of the disk was illuminated by lamplight, the But on other by daylight. increasing the saturation of the hues of the central disks and adding peripheral rings of the same hues, I succeeded in making the hues the same on both sides of the photometer ring. If equality of hue can be obtained when the photometer is illuminated, on one side by lamplight and on the other by daylight,

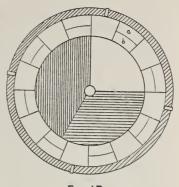


Fig.17.

then the contrast-colors may be brought to the same hue when the photometer is illuminated on one side by a candle or petroleum flame and the other side by the electric arc light or by the whitest Welsbach incandescent lamp.

With a change of distance of the petroleum flame from the photometer the differences in the illumination of the portions a and b, fig. 17, of the ring were changed. When the two sides of the ring were equally illuminated the rings a and b appeared indistinguishable, fusing into one ring of uniform tint and illumination, of the breadth of a + b.

With the best Bunsen photometer disk\* I was unable to decide where it received equal illumination on its sides, so difficult was it to judge of equal brightness of the blue and orange on one side when compared with the orange and blue in the same respective positions on the other side of the disk.

With a petroleum flame of 40 candle light giving power on one side of the rotating photometer and a candle on the other, the delicacy of the indications of the rotating photometer equalled, and even slightly excelled, those of the very best Bunsen photometer disk.

If we bring in succession the translucent sectors of the rotating photometer disk between two lights we observe that, on certain sectors, a and b appear as one surface of the same uniform tint and illumination; on other sectors sometimes a, sometimes b, is the brighter. Rotation of the disk entirely destroys such slight differences and the disk then acts as if made of absolutely homogeneous material, placed in the same conditions of contact of the layers of paper, in each translucent sector.

\* The best Bunsen photometer disks I have used are those sold by the American Meter Company of N. Y. They are made in England.

## 20 Mayer—Phenomena of Simultaneous Contrast-Color,

The hue of the light of "a white incandescent Welsbach lamp" compared with daylight.—When the screen, fig. 1, is illuminated on one side by the Welsbach lamp and on the other by daylight, the side of the ring of the screen facing the daylight appears a feeble blue decidedly tinged with violet. The side of the ring facing the Welsbach lamp is colored greenish orange. This greenish orange was matched in hue, but not in luminosity, by a rotating disk having 41.5 parts of red lead, 41.5 of chrome yellow and 17 of emerald green, viewed illuminated by daylight. This appears to be the hue of the Welsbach light when compared with daylight.

Experiments in which are compared the hues of the light of an incandescent Welsbach lamp and of candle light.—When "a white-light incandescent Welsbach lamp" is placed on one side of the large screen, fig. 1, and a candle, or petroleum flame, on the other side, the cardboard ring of the screen facing the Welsbach light appears of a light bluish green; the side of the ring facing the candle, or petroleum flame, appears of a light carmine.

Matching these hues on the rotator with split disks gave the following results when the two sides of the screen were equally illuminated. The hue of the ring on the side facing the Welsbach lamp was matched by 8 parts of emerald green, 10 of cobalt blue, 25 of ivory black and 57 parts of white Bristol board, as seen illuminated by the Welsbach lamp. The hue on the side of the ring facing the candle or petroleum flame was matched by 12 of carmine, 17 of ivory black and 71 of white cardboard, as seen illuminated by the petroleum flame.

Experiments with the rotating-photometer disk placed between the Welsbach lamp and the petroleum flame.—On rotating the photometer disk, without any central disks, between these lights, the same hues as those already described were seen on its sides, only these hues were much less saturated.

The white disks placed on the sides of the rotating photometer made the hues less saturated.

With a white disk on the petroleum flame side and a black disk on the Welsbach lamp side the difference between the hues of the sides of the photometer were more pronounced.

With a disk of cobalt blue, emerald green and white on the Welsbach-light side and a white disk on the petroleum flame side, the side of photometer facing the Welsbach lamp appeared white and the side facing the petroleum flame was less carmine; the differences in hue being less than in any of the previous experiments.

By trial I found that when a disk of 33 parts of emerald green, 42 of cobalt blue and 25 of white was placed on the Welsbach lamp side of the photometer disk, with a ring of the same hue on the periphery and a disk of 75 parts of carmine and 25 of white was on the petroleum flame side of the photometer disk, with a ring of the same hue on the periphery of the photometer, that the sides of the photometric ring of the photometer had the same hue; which was white tinged with just a perceptible carmine.

We are now in condition to make an interesting experiment which shows in a striking manner the effects of the colored central disks and peripheral rings on the colors of the photometric ring of the photometer. The exact balance of hue on both sides of the photometer has been obtained. Reverse the photometer disk with its central disks and rings and rotate the disk in front of the mirrors. We now see the photometric ring with strong contrast of color on its sides, and the concentric rings a and b are separately seen, not appearing indistinguishable as in the previous experiment. By the reversal we have, by the effects of the disks and rings, added to the effects produced alone by the lights.

It is to be noted that the colors on the disks and rings of the photometer must not be too saturated in hue. The elementary disks of these compound color disks should be made of thin Bristol board and after they have been painted should be well flattened before they are slit radially. After the proper hues have been obtained for the disks which correct the color of the photometric ring, the same hues should be painted on single disks, which are subsequently flattened. The thinner the color-correcting disks and the closer they fit to the photometer disk the greater is their contrast color-effect. The colored rings must be cut out of the painted cardboard, for if the rings are painted after they are formed it is very difficult to make them flat.

To render easy the making of this photometer I made experiments so that one could get the proper hues of the correcting disks and rings by mixtures of definite weights of the pigment powders and definite volumes of gum-water; but it is less troublesome to paint a few disks with colors variously saturated and repeat the experiments I have described, and thus furnish oneself with the sets of disks and rings necessary for the photometric measures of the arc electric light, of the Welsbach white burner, etc., when compared with the standard candle or petroleum flame.

The rotator on which the photometer-disk is revolved should be made as shown in fig. 18, so that the standard, S, and the pulley, P, which is driven by the wheel, W, shade as little as possible the rotating disk.

Photometric measures with the Rotating-Disk Photometer. -On one side of the photometer was placed "a white Wels-

# W. P. Headden-Kehoeite, a new Phosphate.

bach burner" with a light-giving power of 33 candles, on the other side a standard candle. As the candle was gradually brought nearer the rotating photometer the illumination and hues of the portions a and b (fig. 17) of the photometric ring approached equality and when the candle was at a certain distance the difference of illumination and hues of a and b become indistinguishable and only a band with a breadth of a+b with a uniform surface was observed on the sides of the photometric ring.

The measures of the intensity of the light of the Welsbach lamp in terms of the standard candle were made by a friend. He made sixteen measures with my Rotating-Disk Photometer and sixteen with the Bunsen Photometer.

The mean of the series of measures made with the Rotating-Disk Photometer differed from the mean of the departure of the maximum and minimum measures from the mean by 1.49 per cent of the mean intensity of the light of the Welsbach lamp.

The mean of the series of measures made with the Bunsen Photometer differed from the mean of the departure of the maximum and minimum meas-

Fig.18. the departure of the maximum and minimum measures from the mean by 5.22 per cent of the mean intensity of the light of the Welsbach lamp.

Hoboken, N. J., April 15, 1893.

# ART. II.—Kehoeite, a new Phosphate from Galena, Lawrence Co., S. D.; by WM. P. HEADDEN.

ABOUT three years ago I received a number of minerals, mostly from the Merritt mine located at Galena, S. D., among which was the material described in this note. The mineral forms seams and bunches in the ore at one point in the mine. The ore is an argentiferous galena carrying zinc blende and iron pyrites. Goslarite occurs at other points in the mine but was not found in the immediate vicinity of this occurrence. The nearest point at which the goslarite was observed was some 500 feet distant.

The material is white, amorphous and insoluble in water, but it yields a small amount of zincous oxide and phosphoric acid to concentrated hydric acetate upon continued boiling. Ammonic



hydrate extracts rather more zinc than the hydric acetate but does not dissolve it to any great extent. Concentrated potassic hydrate as well as the dilute hydric salts, i. e. HCl. HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> dissolve it readily and completely. The washed mineral forms an impalpable powder with a specific gravity of 2.34 at  $15^{\circ}$ ; it is infusible, and in the closed tube yields an abundance of water. With soda on charcoal it gives an incrustation of zinc oxide, obtained with some difficulty and reacts for alumina, when moistened with cobalt solution. Borax and phosphorus salt dissolve it readily; the beads are slightly yellow while hot and colorless when cold. The saturated beads become opaque upon flaming.

The strongly ignited mineral is not completely soluble in HCl, HNO<sub>3</sub> or in aqua regia; the residue insoluble in these acids contains alumina and zinc, but no phosphoric acid or only traces of it. The air dried material loses when dried at 105–110°, 14.2 per cent and loses but 3.34 per cent additional between 115–120°. It required continued heating over a Kellogg burner to expel the last portion of water. The washed and air-dried material had the following composition:

	I.	II.	III.
Insoluble	1.76	1.78	1.74
H <sub>2</sub> O	- 31.06	31.04	30.95
P <sub>2</sub> O <sub>5</sub>	- 26.76	26.74	26.78
SÓ,	50	•54	
ZnÖ	- 11.64	11.54	11.58
CaO		2 90	
Al <sub>2</sub> O <sub>3</sub>	24.84	25.62	
Fe <sup>2</sup> <sub>2</sub> O <sup>3</sup> <sub>2</sub>	78		
MgO <sup>°</sup>			
Cl		trace	
	100.02	100.16	

Analysis No. I gives after deducting the insoluble-

-	Ŷ					
H <sub>0</sub> O	31.60 =	0.2808	·2808	8.91	9	27
$P_2O_5$ $SO_3$		$0.1529 \\ 0.0031 $	·1560	4.96	5	15
ZnO CaO		$\left. \begin{array}{c} 0.0232\\ 0.0079 \end{array} \right\}$	·0314	1	1	3
MgO		0.0003) 0.1178)	.1909	9.09	4	10
$\operatorname{Fe}_{2}^{2}\operatorname{O}_{3}^{3}$		0.0024 ζ	·1202	3.83	4	12
	99.94					

The oxygen ratios correspond to  $3RO + 4R_2O_3 + 3P_2O_6 + 27H_2O_6$ , or  $R_sP_2O_s + 2Al_2P_2O_8 + 2Al_2(OH)_6 + 21H_2O$  in which

 $R = Zn_{\frac{3}{4}} + Ca_{\frac{1}{4}}$ . The small amount of SO<sub>3</sub> present and the deportment of the material toward concentrated hydric acetate indicate the absence of any significant quantity of basic sulphate or hydrated oxide of zinc. The analyses show an excess of basic oxides over the quantity required by the P<sub>2</sub>O<sub>5</sub> present in order to form neutral salts, and the fact that igniting the material rendered a part of it insoluble may be interpreted in the same sense, especially as the insoluble portion is quite free from phosphoric acid and consists largely of alumina. On the other hand the presence of zinc and phosphoric acid in the hydric acetate solution is suggestive of the presence of a zincous phosphate.

As a control on the water determination, a portion of the unwashed mineral which had been kept for upwards of three years in a stoppered but unsealed bottle, and then exposed to the atmosphere of a warm room for three days, was ignited and showed a loss of 31.48 per cent. I could not detect any  $CO_2$  in the mineral.

The formula suggested, when R=Zn, requires :  $P_2O_5$  27.25,  $Al_2O_3$  26.10. ZnO 15.67 and  $H_2O$  31.09.

The relationship of this mineral is not evident. If, however, the analysis made by Hermann on material from Richmond, Mass., and given on p. 178, Dana's System of Min., 5th ed., is correct, then there is an aluminic phosphate having the formula  $Al_2P_2O_s+9H_2O$  and the material presented in this note may be a molecular combination of the following character:  $2(Al_2P_2O_s+9H_2O)+2Al_2(OH)_6+(Zn_3P_2O_s+3H_2O)$ .

I propose Kehoeite as the name of this mineral, after Mr. Henry Kehoe, to whom I am indebted for the material and who was the first to observe its occurrence.

Note on Jarosite.—This mineral is found as a coating in and sometimes partly filling larger cavities in the auriferous quartzite which is the chief ore obtained in the Buxton mine, Lawrence Co., S. D. It also occurs in the smaller cavities of the rock and in distinct crystals associated with small quartz crystals which cover old fracture-planes in the rock. The jarosite where it is free from limonite has a golden yellow color and the mass is composed of scales which under the microscope appear as six-sided plates. The largest crystals observed were about  $2^{mm}$  in breadth and have a light brown color; their form could be recognized with the aid of a good magnifier as a combination of a rhombohedron and the basal plane.

The purest material that I could select gave :

Quartz	6.10	Quartz ded				
SO <sub>3</sub>		30.29	=	·1817 ·0087	.1004	12
As <sub>2</sub> O <sub>5</sub>	2.36	2.51			∫ 150 <del>4</del>	<i>يد</i> 1
Fe <sub>2</sub> O <sub>3</sub>		49.28		·1478	.1478	9.35
CaO	•39	•42		.0012		
Na <sub>2</sub> O	4.35	4.62			·0158	1
K,0	1.47	1.57		.0027	)	
H <sub>0</sub> O	10.55	11.24		·0999	·0999	6.3
•						
	99.95	99.93				

The excess in O ratios for the iron and water is to be attributed to the presence of some ferric hydrate and the O ratios for the sample is 1:9:12:6.

State School of Mines, Rapid City, S. D.

### ART. III.—On the Ammonium-Lead Halides; by H. L. WELLS and W. R. JOHNSTON.

It is a well known fact that the ammonium double halides, like other ammonium salts, are usually analogous to those of the alkali-metals, especially to those of potassium. For example, in connection with an investigation of the cæsium-mercuric halides, made by one of us,\* it was noticeable that cæsium compounds were prepared, corresponding to all of the four types of ammonium-mercuric halides that had been previously described.

A study of the cæsium-lead and potassium-lead halides has recently been made in this laboratory,<sup>+</sup> and, in view of the fact that the existence of four very simple types of double salts was established by that investigation, it seemed desirable to reinvestigate the ammonium-lead halides, since a considerable number of these with very complicated formulæ had been described. These peculiar ammonium-lead halides have formed the most noticeable exception to the similarity of the alkalimetal and ammonium salts, and it seems probable that it was chiefly on account of these that Remsen has remarked :<sup>‡</sup> "The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own."

All of the extremely complicated ammonium-lead salts have been described by André.§

The list of his alleged compounds is as follows:

\* This Journal, xliv, 221.

† This Journal, xlv, 121.

‡ Am. Chem. Jour., xi, 296.

§ Compt. Rend., xcvi, 435 and 1502; Bull. Soc. Chim., [2], xl, 14.

PbCl, 18NH Cl.4H O PbCl, 10NH Cl.4H O 2PbCl, 18NH Cl.3H O PbCl, 6NH Cl.3H O 4PbCl, 22NH Cl.7H O 4PbCl, 18NH Cl.5H O 4PbCl, 18NH Cl.5H O 2PbBr<sub>2</sub>.14NH<sub>4</sub>Br.3H<sub>2</sub>O PbBr<sub>2</sub>.6NH<sub>4</sub>Br.H<sub>2</sub>O 7PbBr<sub>2</sub>.12NH<sub>4</sub>Br.7H<sub>2</sub>O 3PbBr<sub>2</sub>.2NH<sub>4</sub>Br,H<sub>2</sub>O

From André's original articles, it appeared that he made no mention of having ever prepared any of his remarkable products more than once, and it seems probable that whenever he obtained a crop of crystals or a precipitate he described it as a new compound, without regarding the number of different substances that it might contain. André operated in two ways. A part of his salts were made by dissolving a lead halide in a hot solution of the corresponding ammonium halide and cooling, while the rest were made by dissolving lead monoxide in boiling solutions of ammonium chloride or bromide. From the products made by the last method he obtained lead oxychlorides or oxybromides by heating them with water in sealed tubes. This peculiarity of these products caused him to remark that all the chlorides made in this way seemed to contain some oxychloride. This is the only evidence of any suspicion on his part that he was obtaining mixtures. In a number of instances André describes his products as "crystalline precipitates," "brilliant plates with pearly lustre," "crystallized bodies" etc, so that it would seem that they should have been pure, but after having repeated his experiments, following his methods as closely as his descriptions permitted, with many variations and repetitions, we are convinced that not one of the salts described by André exists.

Our work has resulted in the preparation of the following series of salts :

Type 2:1	Type 1:1	Type 1:2
(NH <sub>4</sub> ),PbBr <sub>4</sub> .H <sub>2</sub> O	$3NH_4PbCl_3H_2O$	$rac{\mathrm{NH}_4\mathrm{Pb}_2\mathrm{Cl}_5}{\mathrm{NH}_4\mathrm{Pb}_3\mathrm{Br}_5}$
(I(II <sub>4</sub> ) <sub>2</sub> I 0DI <sub>4</sub> .II <sub>2</sub> O	$\mathbf{NH}_{4}\mathbf{PbI}_{3}.\mathbf{2H}_{2}\mathbf{O}$	

For comparison, the potassium series, already referred to, is given:

Type 2:1	Type 1:1	Type 1: 2
	3KPbCl <sub>s</sub> .H <sub>2</sub> O	KPb <sub>2</sub> Cl <sub>5</sub>
K <sub>2</sub> PbBr <sub>4</sub> .H <sub>2</sub> O	3KPbBr <sub>s</sub> .H <sub>s</sub> O	KPb Br
* 1 *	KPbBr <sub>s</sub> .H <sub>2</sub> Ö	
	KPbI <sub>3</sub> .2H <sub>2</sub> O	

It is to be noticed that the two series correspond exactly, except that no ammonium-lead bromide of the 1:1 type was

obtained. These results show that the ammonium-lead halides are entirely analogous to the potassium salts, and that there is no indication that they are governed by a law of their own.

Returning to the mixtures described as compounds by André, it should be noticed that he came near finding the correct formulæ for three salts. His formula  $4PbCl_22NH_4Cl$ .  $6H_2O$  would be correct if the water were omitted. He should have found two more molecules of  $NH_4Br$  in the formula  $7PbBr_2.12NH_4Br.7H_2O$  in order to have the salt  $(NH_4)_2PbBr_4$ .  $H_2O$ , and his formula  $3PbBr_2.2NH_4Br.H_2O$ , in comparison with the errors involved in his more complicated mixtures, is rather near  $NH_4Pb_2Br_4$ .

Such work as André's is liable to hinder the development of correct chemical theories. A case has been mentioned above where it is probable that his results have been an important factor in causing the ammonium double halides to be looked upon as a class of bodies distinct from the alkali-metal compounds, and it may be mentioned that Carnegie\* has used André's formula PbBr<sub>2</sub>.6NH<sub>4</sub>Br in support of a theory on double halides, although, as must be added, he considers André's more complicated formulæ as inconsistent with his ideas.

We have investigated the ammonium-lead halides by methods which are entirely like those used for the potassium salts, and, in addition, numerous experiments have been made in order to investigate André's methods of preparation. The analytical methods used have been simple. Ammonium was determined by distillation with potash solution and alkalimetry. Lead was determined by treating the substance in a platinum crucible with sulphuric acid, evaporating, igniting and weighing lead sulphate. To determine a halogen, the substance was treated with hot water and an excess of silver nitrate was added; after sufficient digestion, nitric acid was added, and when the precipitate had settled properly it was collected and weighed on a Gooch filter. Water was determined by the loss at 100°, or sometimes at a somewhat higher temperature.

1:1 Ammonium-Lead Chloride,  $3NH_4PbCl_s$ ,  $H_2O$ :—This is formed by dissolving lead chloride in hot concentrated solutions of ammonium chloride and cooling. Sample A was made by dissolving  $25^{\text{g}}$  of PbCl<sub>2</sub> in 700<sup>cc</sup> of an ammonium chloride solution which was more than saturated when cold. The double salt was deposited in the form of colorless, transparent, prismatic crystals while the solution was still somewhat warm. Some of the crystals were removed from the warm solution, quickly pressed between smooth filter-papers and air-dried for analysis. On cooling the solution, ammonium chloride crystallized upon the double salt. Sample B was obtained by dissolv-

<sup>\*</sup> Am. Chem. Jour., xv, 11.

ing  $5^{g}$  of PbO in 200<sup>cc</sup> of a boiling solution of NH<sub>4</sub>Cl which was nearly cold-saturated. The last method was suggested by André's experiments.

	А	В	$3NH_4PbCl_3.H_2O$
Ammonium	5.22 - 5.45		5.33
Lead	61.12-60.60	61.84-61.88	61.31
Chlorine	31.78 - 31.79	31.64	31.56
Water	1.78		1.78

The water in A was determined by heating at about 120° for one hour. The limits of the conditions under which this salt is formed are narrow, for, on slightly diluting the solutions which have given it, the following compound is produced.

1:2 Ammonium-Lead Chloride,  $NH_4Pb_2Cl_5$ :—This salt is produced under wide limits of conditions. It forms colorless, short, transparent prisms which are usually doubly terminated and are apparently orthorhombic in form. The crystals retain their luster on drying and are anhydrous.

Four crops were made under the following conditions:

	$NH_4Cl$	$PbCl_2$	Volume.
$\mathbf{A}$	$100  {\rm g}.$	30 g.	1000 <sup>cc</sup>
В	100	20	1000
$\mathbf{C}$	200	15	550
D	200	60	700

These crops gave the following analyses:

	Ammonium.	Lead.	Chlorine.
A	2.36 - 2.67	67.38 - 67.36	29.08 - 29.14
В		$66 \cdot 26 - 67 \cdot 56$	
С		66.94 - 66.76	29.16 - 29.24
D		68.00 - 67.28	
Calculated for ( NH <sub>4</sub> Pb <sub>2</sub> Cl <sub>5</sub> )	2.95	67.93	29.12

Another double chloride was observed, the composition of which was not determined. It will be referred to beyond, under the discussion of André's products.

2:1 Ammonium-Lead Bromide,  $(NH_4)_2PbBr_4H_2O:$ — This salt is easily prepared by dissolving lead bromide in concentrated solutions of ammonium bromide. Its formation was also observed when lead oxide was dissolved in ammonium bromide by boiling. It forms beautiful radiating groups of highly refracting, slender prisms. Three crops were made as follows:

	$NH_4Br$	$PbBr_2$	Volume.
Α	200 g.	50 g.	380 <sup>cc</sup>
В	?	25	260
С	200	50	380

The analyses were as follows:

Ammonium.	Lead.	Bromine.	Water.
A 6.01-5.86	37.12 - 36.84	55.06 - 55.10	2.60
В	37.06 - 36.94	54.94	
С	37.26		
Calculated for $(NH_4)_2PbBr_4H_2O$ 6.17	35.63	55.08	3.10

1:2 Ammonium-Lead Bromide,  $NH_4Pb_2Br_5$ :—On slightly diluting solutions from which the preceding salt would be deposited, this salt is obtained. Repeated trials were made to obtain a 1:1 salt intermediate between the two, but these were without success. The salt forms square plates, often several millimeters in diameter. The crystals darken somewhat on exposure to light, but they do not lose their luster on drying, and are evidently originally anhydrous. The compound is formed under rather wide limits of conditions. A single sample was analyzed.

	Found.	Calculated for $ m NH_4Pb_2Br_5$
Ammonium	2.17 - 2.17	2.16
Lead	$49 \cdot 26 - 49 \cdot 12$	49.76
Bromine	48.28 - 48.22	48.08

1:1 Ammonium-Lead Iodide,  $NH_4PbI_3.2H_2O$ :—This was the only double iodide obtained, although a thorough search was made for other salts. It forms hair-like crystals of a pale yellow color. Sample A was made by disssolving  $100^{\circ}$  of  $NH_4I$  and  $10^{\circ}$  of PbI<sub>2</sub> in sufficient hot water to make a volume of  $108^{\circ\circ}$ , and cooling. Sample B was obtained by slightly diluting the solution which gave A. It was noticed that where lead iodide was deposited from a moderately concentrated hot solution of ammonium iodide, the lead iodide disappeared on cooling and in its place was formed a compact, silky mass of crystals. Sample C was such a crop as just described, which was carefully separated from the usual form of the double salt which formed above in the solution.

	А	В	С	Calculated for NH <sub>4</sub> PbI <sub>3</sub> .2H <sub>2</sub> O
Ammonium .	2.40 - 2.25	2.97 - 2.97		2.80
Lead	31.08-31.46	31.36 - 31.20	31.76	32.24
Iodine	59.76 - 59.70	59.85 - 59.75	62.45	59.36
Water	5.60	5.65		5.60

## On André's Products.

André prepared some of his most complicated products, such as 2PbCl<sub>2</sub>.18NH<sub>4</sub>Cl.3H<sub>2</sub>O and 4PbCl<sub>2</sub>.22NH<sub>4</sub>Cl.7H<sub>2</sub>O, by dis-

solving lead chloride in ammonium chloride solutions and by the use of the corresponding bromides. On repeating his experiments with the bromides, we have not observed anything which did not correspond to the salts which we have described, or to mixtures of these with ammonium bromide. He describes his product 4PbCl,.22NH, Cl.7H, O as an abundant precipitate of very brilliant plates with a pearly luster. We have often observed this beautiful precipitate, but, after many attempts, we have been unable to determine its composition with certainty. It apparently forms only in warm solutions which are almost saturated with ammonium chloride. The prismatic salt NH<sub>4</sub>Pb<sub>2</sub>Cl<sub>5</sub> is usually deposited just before the plates begin to form, and it often forms with them. Large amounts of ammonium chloride often crystallized out when attempts were made to separate the precipitate from the motherliquor. This happened often even when the solution with the suspended precipitate was poured upon a large mass of filterpaper, so as to soak up the liquid as quickly as possible. Such a crop, which was granular and showed little evidence of being composed of plates, gave 30.50 per cent of lead. By collecting the precipitates, in the manner just described, at an earlier period in the process of their formation, we succeeded in obtain-ing crops that were apparently pure, but the plates were so exceedingly thin and small, and the mother-liquor was so concentrated, that we had little confidence in the purity of these products. Two such crops gave 51.13 and 53.69 per cent of The formula  $(NH_4)_2$  PbCl<sub>4</sub> requires 53.77, and it is poslead. sible that this may be the true formula for the substance. It is certain that these two products were practically free from the prismatic salt NH<sub>4</sub>Pb<sub>5</sub>Cl<sub>5</sub>, so that it can be positively stated that the ratio of ammonium to lead cannot be greater than 2:1 in this compound. André's formula is, therefore, very far from correct. He must have analyzed a mixture of the plates with ammonium chloride. We have found all such mixtures to be anhydrous after being dried in the air for a short time, hence the water in André's formula is remarkable.

A number of attempts were made to obtain the compound in a purer state by warming the solutions and by diluting them slightly, after the precipitates had formed, but these operations left the products open to suspicion, since it was found that further dilution completely decomposed the plates. Several crops, made in this way, gave 59 01, 57.64, 53.69 and 57.80 per cent of lead, which is an insufficient amount for the 1:1 anhydrous salt, requiring 62.4. This may be its composition, but it is possible also that it is a dimorphous form of  $NH_4Pb_2Cl_3$ , for the plates, in being square with diagonal markings, resemble the salt KPb<sub>2</sub>Br<sub>5</sub> and other bromides of this type. The undetermined double chloride can be readily prepared by dissolving  $160^{g}$  of ammonium chloride and  $25^{g}$  of lead chloride in sufficient boiling water to make a volume of  $400^{cc}$ , and allowing the solution to cool slowly. The compound often forms in such abundance as to completely fill the solution with a loose mass of the very thin plates.

Andre's other method of preparing his products was by dissolving lead monoxide in ammonium chloride and bromide He describes only one complicated bromide. solutions. PbBr, 6NH, Br.H, O, made in this way. We have made a number of experiments with ammonium bromide and lead oxide without obtaining anything but our own salts and mixtures. Since a number of his chlorides were made by dissolving lead oxide in ammonium chloride solutions, we have made a very careful study of the products obtained by this operation. André sometimes indicates the length of time of boiling the ammonium chloride solution with lead oxide, but is uncertain how rapidly he boiled his solutions. We have therefore made numerous experiments with wide variations in the amount of ammonia boiled off. Among the various products that we obtained, including the salts that we have described, we frequently noticed a substance that appeared to be new. It was deposited after the solutions had become cold or nearly so. forming brilliant crystals, apparently nearly cubic in form, but so much rounded as to have no distinct faces. These crystals were often 1 or 2<sup>mm</sup> in diameter. They formed upon the bottom and sides of the beaker, adhering firmly to the glass, and their quantity was sometimes such that the walls of the vessel were thickly studded with them. This product evidently corresponded with one of André's, for he says of "PbCl, 18NH, Cl.4H,O" that it is a very hard crystalline deposit adhering to the glass. We encountered considerable difficulties in obtaining the substance in a pure condition, for it was inclined to deposit upon other things that had previously formed, and it adhered to them as well as to the glass. The first crop analyzed (No. 1) was evidently not pure. Two other crops (2 and 3)appeared better, but still not quite pure. At least, by decanting a solution just before these crystals began to form, we obtained a crop (No. 4), that seemed entirely satisfactory. The following analyses of the four crops were made:

	Ammonium.	Lead.	Chlorine.
No. 1,	<b>28</b> ·28	13.44	58.05 = 99.77
No. 2,		6.51	
No. 3,		6.74	
No. 4,		1.08	

The crystals of the last product had exactly the same appearance as the others. It is evident that lead is not an essential 32

constituent of the substance, and that the substance is ammonium chloride crystallized in an unusual form. Analysis No. 1, corresponds to PbCl<sub>2</sub>.24NH<sub>4</sub>Cl. This is not far from André's formula and it shows what he probably analyzed. It is to be noticed that, while our impure ammonium chloride was practically anhydrous, André gives a considerable amount of water in his formula. It seems probable that he did not properly dry his products before analyzing them, and, moreover, he evidently determined water from the deficiencies in his analyses. There is more or less water in every one of his formulæ.

Since it was evident that André's operation of boiling ammonium chloride solutions with lead oxide could be imitated, with possibilities for greater variations, by adding ammonia to solutions of lead chloride in ammonium chloride, we have carried out a series of experiments on that plan. No indications of the existence of any of André's complicated compounds were obtained in this way, but, besides the form of ammonium chloride that adheres to the glass, a peculiar modification of it in the form of large, transparent pointed crystals with no distinct faces was observed. A sample of these contained 3.23 per cent of lead. When much ammonia was used in these experiments, an oxychloride of lead was obtained. A pure product of this was prepared by saturating a cold-saturated solution of ammonium chloride with lead chloride while boiling, then adding an equal volume of the cold-saturated ammonium chloride solution and finally adding a large excess of ammonia. A precipitate was formed and re-dissolved by the ammonia. The oxychloride was deposited on cooling, in the form of small, blade-like, transparent crystals. Analysis showed that it was the compound PbClOH.

	Found.	Calculated for PbClOH.
	round.	1 001011.
Lead	79.17	79.77
Chlorine	14.06	13.68
Oxygen	[2.72]	3.08
Water	ີ4∙05 <sup>¯</sup>	3.47

This compound has long been well known, having been used as a white pigment. It is worthy of remark that André redescribed this body correctly in one of his papers that has already been referred to.\* He made it by heating a small quantity of "PbCl<sub>2</sub>.6NH<sub>4</sub>Cl.H<sub>2</sub>O" with water in a sealed tube. It is evident that such a product could not have been produced if the chlorides had not contained some basic substance.

\* Bull. Soc. Chim., II, xl, 15, (1883).

### Experiments with Ammonium Choride and Lead Iodide.

Poggiale\* and Völkel+ have each described a mixed double halide of ammonium and lead, neither of which agrees with the types of unmixed halides which we have described in this article. Poggiale's formula is PbI, 4NH, Cl.2H, O, while Völkel's is PbI, 3NH Cl. It is evident that the two investigators obtained the same compound, for both made their products in essentially the same way, and both describe them as occurring in the form of silky needles. We have repeated the experiment of dissolving lead iodide in ammonium chloride solutions and have readily obtained the silky crystals. The product resembles exactly the salt NH, PbI, 2H, O, except that it is considerably paler in color than the latter. An analysis of a pure product, carefully dried by pressing with paper, showed that the formulæ of both Poggiale and Völkel are incorrect, and that their products must have been contaminated with ammonium chloride. The salt corresponds in type to our double iodide. It loses one molecule of water on exposure to the air for two or three days, becoming much darker in color; the second molecule of water goes off at 100°.

		Calculated for
	Found.	$\rm NH_4Cl.PbI_2.2H_2O.$
Ammonium	3.33	3.27
Lead	34.83 - 34.68	37.60
Chlorine	5.11- 5.10	6.42
Iodine	51.08 - 50.94	46.14
Water	5.35	6.54

The analysis indicates that the lead iodide and ammonium chloride do not combine quite unchanged, and that the formula  $NH_4Pb(Cl,I)_{a}$ ,  $2H_2O$  possibly expresses the composition of the product better than the one given above. In the course of our experiments with ammonium chloride and lead iodide, we obtained a crop of crystals which showed an almost complete replacement of the iodine by chlorine. The salt was a 1:2 compound, a type which apparently does not exist among the double iodides of lead. It gave the following analysis:

	Found.	Calculated for NH₄Pb₂Cl₅
Ammonium		2.95
Lead	66.82	67.93
Chlorine	28.76	29.12
Iodine	1.44	

The view that certain mixed lead double halides are to be considered as variable mixtures of two isomorphous, unmixed

\* Compt. Rend., xx, 1180. Am. JOUR. SCI.—THIRD SERIES, VOL. XLVI, NO. 271.—JULY, 1893. double halides was arrived at by Wells and Wheeler\* from experiments with cæsium chloride and lead bromide. Hertyt has more recently arrived at the same conclusion from his investigation of the mixed double bromide and iodide of potassium and lead. It is not safe to conclude, however, because definite mixed double halides do not occur in some cases, that they are never formed. It is certain that there is a tendency toward the formation of such definite compounds in many cases. For example, it is to be noticed that in the above analysis of NH<sub>Cl</sub>PbI<sub>2</sub>H<sub>0</sub>O there is only a slight variation from the composition required by the formula, while, from a solution of the same ingredients, another type of salt was deposited which was almost free from iodine. The compound Cs. HgCl. I., ‡ described by one of us, is evidently a definite mixed double halide which is not intermediate in its properties between the corresponding chloride and iodide, and which has a constant composition. A number of other cæsium-mercuric halides were described, which approached a constant composition when made under varying conditions.

Sheffield Scientific School, March, 1893.

## ART. IV.—On the Rubidium-Lead Halides, and a Summary of the Double Halides of Lead; by H. L. WELLS.

THE cæsium-lead and potassium-lead halides have already been studied in this laboratory, and an account of the ammonium compounds is given in the preceding article. It has therefore seemed desirable to make an investigation of the rubidium salts in order to make the work more complete.

2:1 Rubidium-Lead Chloride,  $2Rb_2PbCl_4$ ,  $H_2O$ :—This was formed by dissolving lead chloride in a solution of rubidium chloride which was so concentrated as to be almost saturated when cold. It forms colorless, transparent, slender, flat prisms which retain their luster on exposure to the air. Two separate crops were analyzed.

	Found.		2Rb <sub>2</sub> PbCl <sub>4</sub> .H <sub>2</sub> O	
Rubidium	29.63	29.85	32.39	
Lead	41.41	41.75	39.20	
Chlorine	26.73	26.84	26.90	
Water	2.29	2.01	1.21	
	100.06	100.45	100.00	

The amount of water in the salt seems somewhat uncertain, but, since there was no evidence of loss of water by efflorescence and since the salt was simply air-dried without being pulverized, the above formula is preferred to  $Rb_2PbCl_4.H_2O$ which requires 2.99 per cent of water. The water was determined by heating to about 200°; at 100° the salt lost only about one quarter of its water in twelve hours.

1:2 Rubidium-Lead Chloride,  $RbPb_2Cl_5:$ —This compound forms small, prismatic crystals which are usually grouped side by side in nearly parallel position. It is produced from solutions which are more dilute than those from which the preceding salt is prepared, and it is formed under rather wide limits of conditions. Two separate crops gave the following analyses:

	Found.		Calculated for RbPb <sub>2</sub> Cl₅	
Rubidium	13.09	12.68	12.63	
Lead	60.57	61.05	61.12	
Chlorine	26.19	26.29	26.22	
,				
	99.85	100.02	100.00	

2:1 Rubidium-Lead Bromide,  $2Rb_2PbBr_4$ .  $H_2O:$ —This salt resembles the corresponding chloride, both in its formation and appearance. Two crops gave the following analyses:

	Found.		Calculated for $2Rb_2PbBr_4.H_2O$
Rubidium	23.17	22.73	24.19
Lead	30.29	30.81	29.29
Chlorine		45.04	45.26
Water	1.55	1.51	1.27
	*	100.09	100.00

1:2 Rubidium-Lead Bromide,  $RbPb_{2}Br_{5}$ :—This forms square plates. It is readily prepared since it is formed under considerable variations of conditions.

Found.	$\begin{array}{c} Calculated \ for \\ RbPb_2Br_5 \end{array}$
9.81	9.50
45.74	46.03
44.62	44.47
100.17	100.00
	9·81 45·74 44·62

1:1 Rubidium-Lead Iodide,  $RbPbI_s.2H_sO:$ —This is the only double iodide that could be produced under widely varying conditions. It forms very slender, hair-like prisms of a pale yellow color. It rapidly loses its water when exposed to the air, undergoing a remarkable change of color. The pale yellow compound quickly assumes an orange color, then the color becomes almost like that of the original salt. It is evident that the salt, which contains two molecules of water, loses a part of this, probably one molecule, with change of color to orange; then the remainder of the water is lost with another change of color. It is interesting to notice, in this connection, that the salt NH, PbClI, 2H, O undergoes a similar change of color, as far as the first step is concerned, on losing one molecule of water when it is exposed to the air, but this salt does not lose its second molecule at ordinary temperatures. A sample of the rubidium lead iodide was rapidly pressed on paper until some of the particles began to show a change of color to orange. Water was determined in this sample from the loss at  $100^{\circ}$ .

	Found.	RbPbI <sub>3</sub> .2H <sub>2</sub> O
Water	6.09	5.02

0-1---1-+--1 6-

An air-dry sample gave the following analysis:

	Found.	Calculated.
Rubidium	13.29	12:70
Lead	28.95	30.73
Iodine	56.80	56.57
	99.04	100.00

#### Summary.

The following table gives a list of the lead double halides which have been prepared in this laboratory. All of them were new compounds except KPbBr<sub>3</sub>.H<sub>2</sub>O and KPbI<sub>3</sub>.2H<sub>2</sub>O, these having been previously described by Remsen and Herty.

4:1	2:1	1:1	1:2
Cs <sub>4</sub> PbCl <sub>6</sub>		CsPbCl <sub>3</sub>	CsPb <sub>2</sub> Cl <sub>5</sub>
Cs₄PbBr <sub>6</sub>		CsPbBr <sub>3</sub> CsPbI	$\mathrm{CsPb}_{2}\mathrm{Br}_{5}$
	2Rb <sub>2</sub> PbCl <sub>4</sub> .H <sub>2</sub> O		RbPb <sub>2</sub> Cl <sub>5</sub>
	$2Rb_{2}PbBr_{4}H_{2}O$		$RbPb_{2}Br_{5}$
	• • • · ·	$RbPbI_{3}.2H_{2}O$	
		3KPbCl <sub>3</sub> .H <sub>2</sub> O	KPb <sub>2</sub> Cl <sub>5</sub>
	$K_{2}PbBr_{4}H_{2}O$	3KPbBr <sub>3</sub> .H <sub>2</sub> O KPbBr <sub>3</sub> .H <sub>2</sub> O	$\mathrm{KPb}_{2}\mathrm{Br}_{5}$
		$\mathrm{KPbI}_{3}.2\mathrm{H}_{2}^{2}\mathrm{O}$	, <b>-</b>

3NH<sub>4</sub>PbCl<sub>3</sub>.H<sub>2</sub>O NH<sub>4</sub>Pb<sub>2</sub>Cl<sub>5</sub>  $\dots$   $(NH_4)_2PbBr_4.H_2O$ NH Pb Br NH.PbI.2H.O NH PbCll. 2H,O

An inspection of the table shows that the cæsium salts differ from the others in including the 4:1 type and in being without any 2:1 salts. It is quite probable that we have not succeeded in preparing all the salts that are possible, but it seems certain that the 4:1 rubidium, potassium and ammonium salts cannot be made on account of the comparative insolubility of the simple halides. The cæsium salts also differ from the others in being all anhydrous. The hydrous rubidium salts have less water or lose it more readily than the potassium compounds. KPbI, 2H, O is stable in the air, but RbPbI, 2H, O loses its water readily. There is evidently a gradation, in affinity for water, from the cæsium to the potassium compounds. A gradation in water, from the chloride to the iodide, apparently exists in the potassium and ammonium compounds of the 1:1 type. That such gradations in water exist among the double halides, increasing with the atomic weight of the halogens and decreasing with the atomic weight of the alkali metals, has already been observed by Remsen.\*

The simplicity of the ratios in the four types of double halides of lead is noticeable. The 4:1 type, according to Werner's remarkable theory,  $\dagger$  may be considered as the ideal type of a double halide of an alkali-metal and a bivalent metal, and as the limit beyond which the ratios of alkali-metal to lead cannot go. The type is represented, as Werner mentions, by numerous double cyanides of bivalent metals, such as K<sub>4</sub>Fe (CN)<sub>6</sub> and by other salts, such as K<sub>4</sub>CdCl<sub>6</sub>.

The number of 2:1 lead salts that we have prepared is rather small, but this is a very common type among the known double halides of the other bivalent metals.

The number of 1:1 lead salts is the largest of all. It is remarkable that all the double iodides belong to this type. This is also a well known type of bivalent metal double halides. It is noticeable that the salt CsPbBr<sub>3</sub> is dimorphous, while three mercuric salts of the same type,<sup>‡</sup> CsHgCl<sub>3</sub>, CsHgBr<sub>3</sub> and CsHgClBr<sub>3</sub> are also dimorphous.

The 1:2 salts are all anhydrous, and a chloride and bromide were prepared with each of the alkali-metals and with ammonium. They are formed under wide limits of conditions and are therefore very easily prepared. It is noticeable that the rubidium, potassium and ammonium chlorides of this type

<sup>\*</sup> Am. Chem. Jour., xiv. 88. ‡ Zeitschr. anorgan. Chem., iii, 281. ‡ This Journal, xliv, 222.

all crystallize in prisms, while all the bromides and the chloride containing cæsium crystallize in plates. A number of other double halides of this types are known, especially among the mercuric compounds. Herty has evidently prepared a potassium-lead double halide of the 1:2 type containing bromine and iodine, although he interprets his results in an entirely different way. In a recent article\* he describes some tabular crystals of an olive green color which he has selected and analyzed with evident care and skill. He gives the following analyses of three separate products :

	Pb	Ι	$\mathbf{Br}$	K
p. 95, D	44.89	17.61	32.59	4.56 = 99.65
p. 95, E	45.42	14.94	34.72	4.50 = 99.58
p. 104,	43.87	22.20	29.03	4.43 = 99.53

The following ratios may be derived from the above analyses:

	Pb.	:	I + Br	:	K
p. 95, D	2.		5.01		1.07
p. 95, E	2.		5.12		1.08
p. 104,	2.		5.08		1.08

The ratio required for the formula  $KPb_{2}(Br,I)_{2}$  is Pb: I+ Br: K = 2:5:1 and the agreement is so close that there can be no doubt that this is the formula. Although no pure iodide of this type has been produced, it is interesting to notice that Herty's compound shows that the potassium salt is capable of existence when mixed with a relatively large amount of the bromide.

Sheffield Scientific School, March, 1893.

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ART. V.—The Galveston Deep Well; by E. T. DUMBLE and G. D. HARRIS.

### The Section.-E. T. Dumble.

THE City of Galveston, Texas, desiring to secure fresh water on the island, if possible, rather than go to the mainland for it, and having failed to do so at moderate depths, decided to sink a well to the depth of three thousand feet unless suitable water was found before going so far. I therefore detailed Mr. J. A. Singley to watch the boring and to secure all the information possible from it.

Work began in April, 1891, and continued with various interruptions and delays until August, 1892. The method used

\*Am. Chem. Jour., xv, pp. 94, 95, 97-99, 103, 104 (Feb. 1893)

-that of revolving and jetting by Chapman Bros., Aurora, Illinois-is fully described by Mr. Byrnes, the contractor, in the Engineering News, August 11th, 1892.

The piping of the finished well is as follows :

15 in	868 feet	868 feet.
12 in	629 feet	1499 feet.
9 in	866 feet	2363 feet.
8 in	75 feet	2438 feet.
7 in	162 feet	2600 feet.
5 in	470 feet	3070 feet.

Many hundreds of samples were taken at the mouth of the well throughout the work and those necessary to show the character and variations of the several beds that were penetrated together with all the fossils collected were carefully preserved and are now in the collections of the Geological Survey of Texas.

Mr. Singley's section, made after a critical study of the specimens taken by him from the well, differs a little from the log of the well-borers as given by Mr. Byrnes in the article referred to and by Prof. Hill in this Journal for November, 1892.\* Therefore, although a part of it has already been published,<sup>†</sup> the entire section is given in a condensed form.

Nos		T'kn's. D'pth
1.	Buffy gray sand	46 - 46
2- 3.	Clay brown and mottled, calcareous concre-	
	tions, etc	
	Sandy clay underlaid by fine gray sand	
6-10.	Alternations of clays and sands containing shells	5
	and fragments of lignite	291-458
	Clayey sands and sandy clays with some mica.	
	Sandy clays with shell fragments	
	Sand and clayey sand	121 - 827
22.	Coarse silvery-gray sand-water bearing	<b>55-</b> 882
	Sandy clay with lignite and few shells	29 - 911
	Indurated coarse gray quartz sand	3 - 914
27 - 28.	Sand and clayey sand, micaceous	118 - 1032
29.	Sandy clay	228 - 1260
30.	Coarse gray quartz sand-water bearing	28 - 1288
31 - 32.	Clay and sandy clay	42 - 1330
33.	Coarse gray quartz sand-water bearing	10 - 1340
34-36.	Clays	44 - 1384
	Coarse gray sand	9 - 1393
	Sandy clays, variously colored	55 - 1448
41 - 43.	Sand, sandy clay and clay	45 - 1493

\* The deep Artesian Boring at Galveston, Texas, p. 426.

+Geological Survey of Texas, Second Report of Progress, Artesian Water by J. A. Singley, p. 78.

Nos		F'kn's. D'pth
44.	Greenish gray sand, micaceous-water bearing	18-1511
45 - 47.	Laminated clays with pebbles, etc., and clayey	
	sand 243	243 - 1754
48.	Cream colored, gritty, calcareous conglomerate	4 - 1758
	Alternations of sand and sandy clays	118 - 1876
54 - 57.	Ditto with lignite, calcareous concretions, etc.	184 - 2060
58 - 59.	Sandy clay and clayey sand	37 - 2097
60-61.	Laminated clay, micaceous sand	56 - 2153
	Greenish clay, indurated gray sand	67 - 2220
64.	Dark clay with lignite, fruits, corals, fish	
	remains, terrestrial and fluviatile shells	29 - 2249
	Clayey sands, shell conglomerate and sand	96 - 2345
71.	Coarse gray sand-water bearing	32 - 2377
72 - 75.	Clays with pyrites, lignite, fish remains and	
	shells. Buff sand—water bearing	55 - 2432
76.	Buff sand—water bearing	11 - 2443
77.	Mottled clay, lignite, fish remains and shells	8 - 2451
78.	Lignite	2 - 2453
79.	Clay, vegetable and animal remains	23 - 2476
	Sand, micaceous in places-water bearing	76 - 2552
84-87.	Alternations of clay and sand	85 - 2637
88-89.	Sandy clay and clayey sand, fossiliferous	80 - 2717
90.	Greenish clay, vegetable and animal remains -	166 - 2883
	Gray sand-water bearing	37-2920
92-93.	Clayey sand and sandy clay	105 - 3025
94.	Sandy clay, micaceous	22 - 3047
95.	Coarse gray sand—water bearing	23 - 3070

The water found in this lowest bed, although apparently less saline than that above it, was not suitable for general use.

While the method of boring employed was not the best for keeping the fossils of each stratum entirely separated from those below it, yet the anchoring of the different sizes of pipe at the depths given has acted as a partial safeguard against the commingling of the faunas of those different zones.

The fossils secured by the untiring watchfulness of Mr. Singley were numerous and varied, comprising many parts of plants, fruits, a pine cone, etc., fish remains and a large number of invertebrate forms. The shells were turned over to Mr. Gilbert D. Harris for examination, and his preliminary report is given herewith.

The results of the investigation add a most important chapter to our knowledge of the history of the formation of the Gulf coast, and furnish a section for reference and comparison which could have been obtained in no other way.

The thickness of the different members of the series as stated by Mr. Harris indicates either a greater dip than we have hitherto supposed to be the case in these deposits or else a greater thickening toward the Gulf. Even at the depth attained the drill has not yet penetrated the sandstones, clays and browncoals of the Fayette Beds as shown at the typical localities in Fayette county, but is still in the sands and limy clays which overlie them.

Although the landward extension of these beds may come today somewhere in the area of the Gulf slope our investigations have, up to this time, failed to bring to light any localities which furnish marine invertebrates of an age later than the Claiborne. So far all the fossils found above that horizon are in fresh water deposits of Miocene, Pliocene, and Pleistocene age, and consist entirely of vertebrates.

#### The Paleontology.—Gilbert D. Harris.

The conclusions drawn from a study of the molluscan remains\* obtained from this well, may be summarized as follows:

1. Of the 11 species obtained from samples numbered from 1 to 10 inclusive, all, except a new form of *Eriphyla*, are recent and well known. In all probability therefore the strata passed through between depths ranging from 0 to 450 feet must be referred to a post-Tertiary or Pleistocene epoch. The small *Eriphyla* will probably be found recent on the Gulf shore.

2. The fauna is so sparse between numbers 10 and 61 inclusive that it is unsafe to attempt to state just where in the upper Tertiary it should be placed. In fact beds included between depths 450 and 1500 may not be Tertiary at all but Pleistocene. The undescribed, and probably for the most part extinct species occurring from depths 1500 to 2150 feet show conclusively that these beds are Tertiary.

3. The fossils obtained from samples numberd 61 to 91 inclusive show that this part of the well section must be referred to the Miocene series. Moreover, it is quite evident that upon the whole the fauna represented is that of the upper rather than the lower Miocene. Out of about 72 species, 26 are still living on the Atlantic or Gulf coast of the United States, while 6 more survive only in the Pacific. Of the 36 new or doubtful forms probably the great majority are extinct, though it is unsafe to predict what will yet be found in the Gulf of Mexico. Arca Carolinensis, Turritella subgrundifera var. Chione, sp. nov. of west Florida Miocene, Terebra, n. sp. of west Florida Miocene may be regarded as characteristic species, leaving no doubt, when taken in connection with the foregoing

\* For a full account of the species obtained see Geol. Surv. Tex., 4th Annual Report.

facts that this portion of the well section belongs to the Miocene series, and in all probability to the upper part of the same.

The above conclusions may be stated diagrammatically as follows:

Sample Nos.	Depth in feet.	Geological horizons.
1-10	46 - 458 .	Pleistocene.
10-44	458-1511 .	Doubtful.
44-61	1511-2153 .	Upper Tertiary.
61-91	2153-2920 .	

Probably some of the strata between the depths of 458 and 2153 feet were deposited in Pliocene times, but not a trace of a species characterizing that series has been found.

ART. VI.—On the Iodometric Determination of the Nitrates; by HIPPOLYTE GRUENER.

[Contributions from the Kent Chemical Laboratory of Yale College-XXIV.]

DE KONINCK and Nihoul\* describe a method for the iodometric determination of nitrates, in which the decomposition of the nitrates is effected by the action of gaseous hydrochloric acid, the gases evolved being passed into potassium iodide; but the method is a cumbersome one In a former paper<sup>+</sup> by Professor Gooch and myself a method was described according to which nitrates were decomposed successfully and easily by a solution of manganous chloride in hydrochloric acid, the products of decomposition being passed into potassium iodide, and the liberated iodine titrated with sodium thiosulphate. The ease with which hydriodic acid has been applied in this laboratory as a reducing agent in the determination of arsenic, chloric and antimonic acids‡ has suggested its application for the same end to nitric acid, and the present paper is the account of attempts in this direction.

The Action of Phosphoric Acid and Potassium Iodide upon Nitrates.-The decomposition of the last traces of nitrates in presence of potassium iodide and sulphuric acid does not occur except at very great concentrations, and, as at great concentrations sulphuric acid in presence of hydriodic acid itself liberates iodine, the use of sirupy phosphoric acid to bring about the required decomposition naturally suggested itself. Various attempts to simplify the process while still registering

<sup>\*</sup> Zeitschr. f. angewandte Chemie. 1890, p. 477.

<sup>†</sup> This Journal, vol. xliv, p. 117. ‡ This Journal, vol. xl, p. 66; vol. xlii, p. 220; vol. xlii, p. 213.

the amount of reduction by arsenic acid in the residue proved futile, and a distilling apparatus was found to be necessary. For this purpose a small retort was used, the neck of which was bent downward about two inches from the body, so that the retort itself might be tipped backward, allowing the unbent portion of the retort to run upward, thus guarding against loss from spattering. Into the tubulature of the retort was ground a glass tube drawn out at both ends to serve as a perforated stopper for the entrance of carbon dioxide. The neck was passed through a rubber stopper into a side-neck Erlenmeyer flask, the exit tube of which was prolonged and dropped into a side neck test tube used as a trap. The retort was covered with a simply contrived hood which kept the upper parts warm and prevented the iodine from settling anywhere. In the retort was placed the nitrate with an excess of potassium iodide, and in the receiver a known amount of decinormal solution of arsenious oxide strongly alkaline with hydrogen sodium carbonate and diluted to a convenient bulk. The trap contained nothing but water. The phosphoric acid used was at first 10 cm<sup>3</sup> of strong acid, specific gravity 1.7, with varying amounts of water, but when it was found that the amount of water present was an essential feature, a definite mixture was used as designated in the tables. The acid was added to the retort last of all and after carbon dioxide had been passed for a sufficient length of time heat was applied. The carbon dioxide was evolved in a Bonn generator from materials which had been carefully boiled, and cuprous chloride was added to the acid in the generator to take up the oxygen from any traces of air. Between the introduction of phosphoric acid into the retort and the application of heat a good stream of gas was passed for ten minutes, at the end of which time the bubbles escaping at the last trap were completely absorbed in potassium hydrate of the requisite strength. The first experiments were in blank with no nitrate present. Upon warming the mixture of phosphoric acid and 2 grm. of the

Upon warming the mixture of phosphoric acid and 2 grm. of the iodide signs of free iodine were developed, and by titration of the contents of the receiver at the end, iodine to the amount of  $\cdot 0014$  grm. was found to have been liberated, either by residual traces of air or by dissociation. The experiment was repeated, but in this case all the water used had been boiled immediately before the experiment and here iodine to the extent of  $\cdot 0009$  grm. only was found to have been liberated. The cause and remedy for this liberation of iodine are discussed presently. A series of experiments was performed to study the action of the reagents when nitrates were present.

The method of procedure was as follows: The nitrate was taken for convenience from a solution of 5 grams in 500 cm<sup>3</sup>

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The iodide was introduced dry or in solution of water. according to the bulk of water allowable. This mixture was boiled a moment to drive out all air, the phosphoric acid was then added, and carbon dioxide was passed as described, the receiver containing the arsenious oxide and the trap being already in position. It had been found that all but a trace of iodine was caught in the first receiver, so that the rubber stopper closing it could do no harm. When large amounts of nitrate were used the clots of solid iodine settling out in the receiver were dissolved by means of a crystal or two of potassium iodide. The solution in the retort was boiled until it was clear that all the iodine had distilled over, and usually until the boiling in the retort had ceased. It was found advisable to empty the retort so soon as it was cool enough, else the phosphoric acid became unmanageable. The retort after each experiment was washed out with ammonia and water.

The results of these first experiments are shown in Table I.

			Water added to 10 cm <sup>3</sup> of phos-			
	KNO3	KI	phoric acid,	$KNO_3$	Error in	Error in
	taken.	taken.	sp. gr. 1.7.	found.	KNO <sub>3</sub> .	$HNO_3$ .
	Series 1.		10		, i i i i i i i i i i i i i i i i i i i	-
	grm.	grm.	cm <sup>3</sup> .	grm.	grm.	grm.
1	0.0002	$\cdot 2$	2	0.0003	0.0004 +	0.0002 +
2	0.0010	$\cdot 2$	2	0.0015	0.0002 +	0.0001 +
3	0.0020	.2	2	0.0051	0.0001 +	0.0001 +
4	0.0020	$\cdot 2$	$\frac{2}{2}$	0.0052	0.0002 +	+ 6000.0 +
5	0.0100	$\cdot 2$	2	0.0093	0.0007 -	$0\ 0004 -$
6	0.0100	$\cdot 2$	$\frac{2}{2}$	0.0103	0.0003 +	0.0002 +
7	0.0500	•3	3	0.0216	0.0016 +	0.0010 +
8	0.0500	•3	3	0.0195	0.0008-	0.0005-
9	0.0200	•3	3	0.0500	$0\ 0005 +$	0.0003 +
10	0.0200	•3	3	0.0500	0.0005 +	0.0003 +
11	0.0200	•5	6	0.0496	0.0004 -	0.0002 -
12	0.0200	.2	. 6	0.0499	$0\ 0001 -$	0.0001-
13	0.0300	•5	4	0.0293	0.0001 -	0.0004-
	Series 2.					
14	0.0616	1.5	1	0.0682	0.0066 +	0.0039 +
15	0.0570	2.5	1	0.0643	0.0013 +	0.0045 +
16	0.1030	1.1	1	0.1061	0.0031 +	0.0018 +
17	0.1062	1.1	1	0.1191	0.0135 +	0.0081 +

TABLE I.

With one or two exceptions the results of Series 1 are fairly good. Those of Series 2 are very bad. The only essential difference between the two series is in the dilution of the phosphoric acid used. In the first series there is always enough water present to make the specific gravity of the phosphoric acid no higher than 1.6 for small amounts of iodide and nitrate, and lower than that number when these amounts are increased. The suggestion is obvious that dissociation of the hydriodic acid may occur at the boiling point of the stronger acid. According to Berthelot\* aqueous solutions of hydriodic acid under pressure begin to dissociate at 275° or even under. The temperature of the retort at the end of an experiment was taken and found to be far beyond the range of a thermometer reading to 360°. It is evident, then, that under the conditions there should be opportunity for dissociation. Four experiments in which potassium iodide was treated with phosphoric acid, specific gravity 1.7, undiluted, gave of liberated iodine caught in arsenious acid .0030 grm. .0044 grm. .0049 grm. .0030 grm. of iodine, corresponding to .0008 grm. .0012 grm., .0013 grm., .0008 grm. of potassium nitrate respectively. These results would account only in part for the errors noted but, they are in the same direction. Chapmant has found that concentrated hydriodic acid acting upon organic nitrates and nitrites reduces them not alone to nitric oxide but even in part to ammonia. The conditions of the experiments in Series 2 approximate to concentration of the hydriodic acid, and the reaction that Chapman found probably takes place here to a limited extent. Concentration of the hydriodic acid then must be avoided, both to eliminate dissociation and excessive reduction of the nitrate.

Therefore the plan was adopted of diluting the solution, so that the temperature and concentration should be effective in decomposing the nitrate, but should not bring about the complications just mentioned. A blank experiment made thus, 18 cm<sup>3</sup> of a solution of phosphoric acid of specific gravity 1.39, being used, gave of liberated iodine only 0004 grm. corresponding to 0001 grm. of potassium nitrate. So that under these conditions we may be assured that dissociation occurs if at all to only a slight extent. In the following experiments, therefore, the nitrate is decomposed in presence of dilute phosphoric acid, the dilution and the quantity taken being included in Table II.

The iodine of 41 was collected in potassium iodide and titrated with thiosulphate. Series 3 requires little special comment. The experiments ran along smoothly, the manipulation was easy, the care required in watching very little and the results are fairly satisfactory. The causes leading to the high results of Series 2 seem entirely eliminated by the dilution. Series 4 is a direct continuation of Series 3, differing in the single point that larger amounts of nitrate are handled. These results with some exceptions are decidedly low. It appears that with a fair percentage of water present, as the amounts of nitrate grew larger, the error became a negative one. The explanation for this seemed to be that the last portions of nitric acid must have

\* Ann. de Chim. et Phys., (IV), xx, p. 392.

4 Journ. of the Chem. Soc., vol. xx, 1867, p. 166.

distilled before decomposition, whenever the original amount was large. Nitric acid was accordingly tested for in the distillate, and to this end all the conditions of the experiment were repeated, except that the receiver contained only water. Of the nitrate 0.4 grm. and of the iodide 4 grm., twice the amount theoretically necessary were put into the retort, and at the end of the experiment the solution in the receiver was boiled with hydrogen peroxide to decompose the hydriodic acid and drive out the iodine, care being taken to keep enough water to hold any nitric acid present. When all the iodine was gone sodium carbonate was added, the solution evaporated and the residue ignited and tested with a saturated solution of manganous chloride in hydrochloric acid, as described in the previous paper above mentioned. By this means 0.0002 grm. potassium nitrate are very easily detected in 10 cm<sup>3</sup> of solution. Nitric acid was found in the distillate of this experiment as well as in two others conducted with 0.2 grm. and 0.1 grm. of the nitrate respectively. The residues in the retorts of these three tests showed no trace of nitric acid.

TABLE II.

				Sp. Gr. of solution of	Amount		
	KNO3	KI		phosphoric	of sol.	Error	Error
	taken.	taken.	Found.		used.	KNO <sub>3</sub>	HNO <sub>3</sub>
Q		tancn,	round.	acia.	usou.	III 03	111403
Series a							
	grm.	grm.	grm.			grm.	grm.
18	0.0200	1.	0.0200	1.43	$17 \mathrm{cm}^3$	0.0000	0.0000
19	0.0500	0.2	0.0201	1.43	17	0.0001 +	0.0001 +
20	0.0500	1.	0.0198	1.43	17	0.0002 -	0.0001 -
21	0.0250	1.	0.0220	1.43	17	0.0000	0.0000
22	0.0300	1.	0.0301	1.43	17	0.0001 +	0.0004 +
23	0.0300	1.	0.0315	1.43	17	$0\ 0012 +$	0.0007 +
24	0.0320	1.	0.0323	1.43	17	0.0003 +	0.0002 +
25	0.0400	1.	0.0409	1.35	20	0.0003 +	0.0006 +
26	0.0450	1.	0.0444	1.35	20	0.0006 -	0.0004-
27	0.0200	1.	0.0499	1.37	20	0.0001	0.0001-
Series	4.						
28	0.0600	1.	0.0568	1.37	20	0.0032-	
29	0 0600	1.	0.0575	1.37	20	0.0025-	
30	0.0600	1.	0.0576	1.37	20	0.0024 -	
31	0.0600	$\overline{2}$ .	0.0288	1.37	20	0.0012 -	
32	0.0600	$\overline{2}$ .	0.0602	1.37	18	0.0005 +	
33	0.0200	$\overline{2}$ .	0.0708	1.37	18	0.0008 +	
34	0.0800	2.	0.0811	1.37	18	0.0011 +	
35	0.0900	2.	0.0842	1.37	18	0.0028-	
36	0.1000	$2 \cdot$	0.0996	1.37	18	0.0004 -	
37	0.1000	$2 \cdot$	0.1012	1.37	18	0.0012 +	
38	0.1000	1.5	0.0909	1.37	18	0.0091-	
39	0.1000	2.5	0.0979	1.37	18	0.0021 -	
40	0.1021	3.	0.1005	1.43	17	0.0016-	
41	0.1032	2.	0.0949	1.43	17	0.0085 -	

The process seems reliable enough, then, for estimating nitrates in small quantities not exceeding an equivalent of 0.04 grm. or 0.05 grm. of potassium nitrate. Every experiment performed with quantities not larger than 0.05 grm. has been given here, except four in which an imperfection in the apparatus showed an obvious mechanical loss. The errors in these experiments lie between the extremes of 0.0016 grm. + and 0.0008 grm. - on the nitrate, with an average error of 0.00016 grm. If series 3 alone is taken, in which the dilution of the phosphoric acid was regulated, we have as extreme errors 0.0012 grm. + and 0.0006 grm. - with a mean error of 0.0002 grm. +. With quantities of nitrate above 0.05 grm. the process does not seem a safe one, inasmuch as with a moderate amount of water present some nitric acid distils over undecomposed, and with little water present other complications as seen above arise.

The method so far as it is applicable may be summed up as follows. The nitrate not to exceed in amount 0.05 grm. of potassium nitrate, is introduced into a retort, together with ten times its weight of potassium iodide, and 17 to 20 cm<sup>3</sup> of phosphoric acid, of specific gravity 1.43. All water used should be recently boiled. Carbon dioxide is passed from a receiver carefully set up. The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, alkaline with a good excess of hydrogen sodium carbonate and diluted to a convenient bulk. To this flask is attached for additional safety a simple trap containing water. The solution in the retort is boiled until it is clear that no more iodine remains, when the receiver, after proper washing and addition of the liquid in the trap, is titrated with iodine to find the amount of arsenious oxide still left. This gives the measure of the iodine evolved and consequently of the nitrate present, according to the equation

### $2HNO_{a} + 6HI = 4H_{a}O + 2NO + 3I-I$

The Decomposition of Nitrates by Antimonious Chloride. —The failure mentioned above, in attempting to use arsenious oxide to register the action of nitric acid, led to the trial of antimonious chloride as a substitute, inasmuch as this substance is easily oxidizable and less volatile than arsenious chloride in presence of hydrochloric acid. This latter fact is of great importance in the decomposition of a nitrate. The point to be tested was whether the complete decomposition of nitrates by the action of antimonious chloride in hydrochloric acid solution, and the absorption of the nascent oxygen to form antimonic chloride would be secured, so that the antimonious chloride left at the end as compared with the amount taken should give the measure of the nitrate used, according to the equation :

#### $3SbCl_s + 2HNO_s + 6HCl = 3SbCl_s + 2NO + 4H_sO.$

Antimony chloride was dissolved in strong hydrochloric acid, and the solution standardized by diluting convenient portions, adding tartaric acid, nearly neutralizing with 25 per cent solution of sodium hydrate, treating with excess of hydrogen sodium carbonate and titrating with decinormal solution of iodine in presence of starch, the blue color being taken as the end reaction.

Known portions of this solution boiled with potassium nitrate for a considerable length of time, then diluted, neutralized and titrated (all a simple quick process), showed oxidation to the extent of about 90 per cent of the nitrate present. The evidence pointed to the conclusion that the nitrate was broken up, but that the residue failed to register the amount of decomposition. The products of decomposition when passed in a current of carbon dioxide into potassium iodide set free iodine, but had no oxidizing effect upon an alkaline solution of arsenious oxide. The conclusion was drawn that nitrosyl chloride was probably given off, which breaking up on contact with water into hydrochloric and nitrous acids exerts no effect upon arsenious oxide in alkaline solution. To see if the nitrosyl chloride was set free in exact measure of the nitric acid lost the following experiments were made.

Into a diminutive retort—made from a pipette shaped like a Liebig's drier and connected by a sliding joint covered by rubber into a Kjehdahl tube used as a receiver, and so placed that carbon dioxide passing through the apparatus should enter from below-lifting the air before it-was introduced the nitrate, dry, washed down with a few drops of recently boiled water, or, if more liquid was required, with hydrochloric acid lest the liquid become too dilute. From a burette a definite amount of antimonious chloride solution, somewhat in excess of the nitrate taken, was introduced. The receiver was charged with 0.25 grm. potassium iodide diluted with recently boiled water and was joined to a trap filled with water. After carbon dioxide was passed through the apparatus for about ten minutes, the solution was warmed on a high boiling bath (103°-107°) to ensure the safety of the retort, to keep the antimony pentachloride from breaking up, to retain the bulk of the acid in the retort and to prevent mechanical loss. This method of procedure was found entirely satisfactory. After fifteen minutes digestion the receiver and trap were washed out and at once titrated with sodium thiosulphate. The residue in the retort was treated exactly as was the antimonious chloride when it was standardized. The solution here must be kept dilute, lest at the great heat caused by neutralizing strong

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solutions there be action upon the pentachloride on the part of the small amount of tartaric acid now present. The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidized by the nitrate, and by difference we have the measure of the nitrate present. The results are given in series I and II. In experiments (1) to (8) the receivers were washed with ordinary distilled water; after that with water recently boiled.

	Series I.					
		KNO3 correspond-	Entire			
	$KNO_3$	ing to I found in	$KNO_3$	Error in	Error in	
	taken.	receiver.	found.	KNO₃.	$HNO_3$ .	
	gram.	grm.	grm.	grm.	grm.	
1	0.0222	0.0020	0.0333	0.0011 +	0.0001 +	
2	0.0336	00.026	0.0333	0.0003 -	0.0002-	
3	0.0410	0.0042	0.0471	0.0001 +	0.0001 +	
4	0.0523	0.0057	0.0554	0.0001 +	0.0001 +	
5	0.0664	0.0016	0.0679	0.0015 +	0.0003 +	
6	0.0759	0.0085	0.0752	0.0002 -	0.0004 -	
7	0.0832	0.0103	0.0841	0.0004 +	0.0005 +	
8	0.0934	0.0113	0.0955	0.0051 +	0.0013 +	
9	0.1034	0.0134	0.1036	0.0005 +	0.0001 +	
10	0.0565	0.0024	0.0259	0.0003-	0.0002-	
11	0.0122	0.0002	0.0130	0.0003 +	0.0005 +	
12	0.0065	0.0003	$0\ 0067$	0.0005 +	0.0001 +	
13	0.0026	0.0001	0.0053	0.0003 -	0.0005-	
14	0.1532	0.0098	0.1221	$0\ 0005 -$	0.0003-	
15	0.1540	0.0146	0.1540	0.0000	0.0000	
16	0.1828	0.0210	0.1865	0.0013-	0.0008-	

Three more experiments were performed to see if the titration of the iodine set free in the receiver could be accomplished as well in alkaline solution by means of arsenious oxide. For this purpose the solutions from the receivers were poured into a strong solution of sodium bicarbonate, care being taken to prevent loss during effervescence.

#### Series II.

17	0.0230	0.0052	0 0533	0.0003 +	0.0002 +
18	0.0541	0.0062	0.0549	0.0002 +	0.0001 +
19	0.0541	0.0063	0.0537	0.0004 -	0.0002 -

The results run from extremes of  $\cdot 0021$  grm. + to  $\cdot 0013$  grm. - with a mean error of  $\cdot 00016$  grm. +, which tends to emphasize the well known fact that it is impossible to remove every trace of air from reagents and generator. The operation is quick, taking in all three-quarters of an hour and requiring very little watching. The experiments given are all that were performed with the apparatus as described, it not having been found necessary to reject a single determination for mechanical mischances.

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, NO. 271.-JULY, 1893.

### 50 G. H. Williams—Piedmontite and Scheelite from the

Neither of the processes described presents in general advantages equal to those of the manganous chloride method to which reference has been made, but under special conditions they may be found useful.

In concluding I would express my thanks to Professor Gooch for valuable advice and assistance given during the course of the investigation.

### ART. VII.—*Piedmontite and Scheelite from the Ancient Rhyolite of South Mountain, Pennsylvania;* by GEORGE H. WILLIAMS.

### [Published with permission of the Director of the U.S. Geological Survey.]

IN a recent paper on the Ancient Volcanic Rocks of South Mountain in Pennsylvania and Maryland, the identification of the manganese epidote, piedmontite, in the acid lavas was incidentally mentioned.<sup>\*</sup> Several points of interest regarding the occurrence, association and chemical composition of this mineral, which deserve a special notice, have been brought out by its subsequent study.

The acid or rhyolite lavas so extensively developed in South Mountain possess a wide range of color, within which varying shades of pink, maroon and purple are conspicuous. These reddish varieties show many signs of being rich in manganese. Aside from their color, clefts in the rock are often stained black by the oxides of this element, while ordinary weathering not infrequently brings about a similar result. In the basic and more highly ferruginous lavas, conditions favorable to the formation of epidote have at some time obtained to an extent rarely surpassed. Amygdules are filled with this mineral, while in some localities the rock itself is fairly changed to a mass of epidote. Throughout their entire extent the basic lavas have been "epidotized" to a remarkable degree. The tendency to epidote formation is likewise apparent in the acid rocks, especially when they are examined under the microscope. According to the supply of manganese present, however, the common epidote shows every graduation from the faintest rose tinge, through the more pronounced pinks of withamite, to the rich deep carmine of typical piedmontite. All of these varieties frequently occur within the limits of a single thin section, or even as an irregular coloring of a single crystal or group of crystals. In such cases, the deepest color is at the center, as though the

\* This Journal, III, vol. xliv, p. 495, Dec. 1892.

growth of epidote had continued, even after the available manganese supply had become exhausted.

The deeply colored, typical piedmontite is irregularly distributed as a microscopic constituent, being most abundant in the reddest rhyolites, and in them, most developed in the feldspar phenocrysts, where it is evidently secondary. At some points a considerable thickness of radiating piedmontite needles occupy cavities and seams in this rock. It is the occurrence of such macroscopic masses of the pure mineral which makes this region an important piedmontite locality; for, while this substance is becoming constantly more widely known as a microscopic rock constituent, the places where it occurs in specimens of macroscopic size and beauty are still very few. In one case piedmontite was found replacing old spherulites and projecting from the sides of ovoid cavities into a mass of enclosing scheelite.

These three types of occurrence will now be described in the inverse order of that in which they have just been mentioned.

1. Minute crystals in scheelite.—In the area of rhyolite breccia mentioned in the writer's former paper as occurring in the Buchanan valley, two miles north of the Chambersburg turnpike,\* a large block of the acid lava was found behind Musser's store, in which fairly well crystallized piedmontite was abundant. The manganese epidote here occurred wholly or partly filling ovoid areas which resemble old spherulites. The rock itself is banded with lines of flow-structure and has a deep red color from the piedmontite disseminated through it.

Associated minerals are quartz and rarely hematite, but the center of the cavity is usually occupied by a white vitreous mineral, into which the terminations of the minute piedmontite needles project, and which, quite contrary to expectation, proved to be *scheelite*.

The projecting ends of these radiating needles, in spite of their minute size, offer the best material yet found for the study of the crystallographic and optical properties of the South Mountain piedmontite. When a little of the white friable matrix is gently pulverized and mounted in balsam for the microscope a very beautiful result is secured. An abundance of sharply defined crystals are seen bounded by the characteristic planes of epidote, but on account of their intense pleochroism exhibiting, when viewed with one Nicol, many tints of yellow, orange, carmine and amethyst. These little crystals, although very sharp and brilliant under the microscope, are rarely over  $0.2^{mm}$  in length and  $0.05^{mm}$  in breadth. They are therefore too small to measure, although some of

\* Loc. cit. p. 492, and map on p. 483.

their characteristic forms, as seen under the microscope are shown in fig. 1. Their elongation, as is usual for all epidotic minerals, is invariably parallel to the orthodiagonal axis.

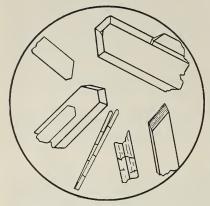


Fig. 1.—Piedmontite needles from scheelite, Buchanan valley, Pa. Magnified  $\times$  150.

Crystals which lie upon their orthopinacoid, as in the figure, are straw-yellow to orange, according to their thickness, when their long direction is transverse to the vibrating plane of the Nicol, and some shade of amethyst when these two directions are parallel. In converged polarized light such sections show an acute positive bisectrix with large optical angle, and optical plane normal to their direction of elongation. Crystals lying on the positive orthodome show the same amethyst shades par-

allel to their longest direction and deep carmine transverse thereto. The pleochroism is therefore a, yellow; b, amethyst; c, carmine, and the absorption: c > b > a, or c > b = a. In terms of Radde's international color scale the tints of the rays vibrating in these three directions were fixed, as nearly as possible, as a=7, s; b=23, l; c=25, m. This pleochroism agrees, except for differences due to variation in the amount of manganese, with that of all other red epidotes as may be seen from the following table:

Locality.	Author.	a	в	c
St. Marcel	Laspeyres	clear orange	amethyst	blood red
Sweden	$\mathbf{Flink}$	orange	violet	carmine
Japan	Koto	deep reddish violet	light violet	brownish red
Groix	Lacroix	yellow	very clear rose	bright rose
Glencoe	Lacroix	lemon-yellow	clear rose	light rose
South Mt,	Williams	yellow to orange	amethyst	carmine

The exception in the case of the Japanese piedmontite as given by Koto, \* does not agree with my own determination upon a number of specimens from Japan received from him. My examinations of the Japanese piedmontite show it to be quite normal, and give: a, yellow; b, pale violet; c, magenta. I also find the absorption not as Koto gives it, a > c > b, but c > b > a.

\* Journal of the College of Science, Imperial University, vol. i, p. 306, 1887.

The determination of the colorless mineral associated with the piedmontite at this locality as *scheelite* was so unexpected that a few words may be devoted to its properties. It is quite brittle and has a vitreous to resinous luster and fairly good pyramidal cleavage. No trace of crystal form was observed, but the cleavage angle measured approximately 100°. In converged polarized light the pyramidal cleavage flakes show a uniaxial figure of positive character and strong double refraction. Moistened with hydrochloric acid the fragments became yellow and then, as the solution dries it becomes a deep blue. Fused with Na<sub>2</sub>CO<sub>3</sub> on charcoal and dissolved in water the solution is a deep blue. The phosphor salt bead is green when hot in the reduction flame, but it remains a deep emerald tint on becoming cold, instead of turning blue as the scheelite bead usually does. The specific gravity determined by a pycnometer with the little material at hand gave 5.61, which, though somewhat low for scheelite, is as good a result as could be expected with the somewhat porous substance.

2. Radiating aggregates filling veins in the rhyolite.—The locality which has furnished the greatest abundance of South Mountain piedmontite is on the west flank of Pine Mountain about one mile north of Monterey station. The mineral has here a deep carmine color and forms spherulitic aggregates of needles upon which no trace of crystal form is visible. They are crowded closely together and fill irregular veins which vary in width from 5 or 6<sup>cm</sup> to the finest possible threads. The average diameter of the radiating aggregates is from 5 to 7<sup>mm</sup>, although occasional needles have been observed measuring as much as 10<sup>mm</sup> in length.

In microscopic section these aggregates present a brilliant appearance. The piedmontite needles have the same optical properties as the more perfect crystals already described; but, since there is no parallelism of their  $\dot{a}$  and  $\dot{c}$  axes, the fibers all show an amethystine color in the direction of their elongation, but various shades of carmine, yellow and orange in transverse directions. Some of the needles show in their pleochroism a complex twinning structure like that figured by Laspeyres.\* The microscope shows further that the needles of these radiating aggregates are minutely intergrown with clear limpid quartz. This mixture is so extremely intimate as to render the obtaining of pure material for analysis very diffi-A powder obtained with the Thoulet solution was carecult. fully analyzed by Mr. W. F. Hillebrand, of the U. S. Geological Survey, with the following result :

\* Zeitschrift für Kryst., vol. iv, Pl. XI, fig. 8, 1880.

	SiO <sub>2</sub>	47.37
	$Al_2 \tilde{O}_3$	18.55
1	$\operatorname{Ce}_{2}^{2}O_{3}^{3}$	0.75
Ì	$R_2 O_3$ (other rare earths)	1.28
`	Fe <sub>2</sub> O <sub>3</sub>	4.02
	$M_{H_{a}}O_{a}$	
	MnÔ <sup>°</sup>	1.92
	CaO	15.82
	MgO	
	K 0	
	Na <sub>a</sub> O	0.23
	H <sub>0</sub> Ô	
	CũO	
	Pb0	0.14
	Total	100.05

The silica is here 10 per cent too high for epidote, but as the microscope showed that the only impurity was pure quartz, it seemed quite justifiable to recalculate the analysis after deducting 10 per cent of this substance. To substantiate this conclusion another separation was attempted with greater care. The piedmontite was very finely pulverized and only that portion used which fell in a solution of methelyne iodide having a specific gravity of 3.32. The microscope showed that there was still a small quantity quartz admixed, although much less than in the preceding instance. A determination of the silica of this powder by Mr. Hillebrand gave 40.08 per cent. It seems therefore certain that the recalculation of the analysis given above on a basis of 37.37 per cent silica would give very nearly the composition of our piedmontite. The result thus secured is as follows:

	SiO <sub>2</sub>	37.37
	$Al_2 \dot{O}_3$	22.07
(	$Ce_2^2O_3^3$	0.89
1	$\mathbf{R}_{2}^{2}\mathbf{O}_{3}^{3}$ (other rare earths)	1.52
C	$Fe_2O_3$	
	$\widetilde{\mathrm{Mn}}_{\mathrm{s}}^{\mathrm{c}_{2}\mathrm{c}_{3}}$	8.15
	MnO <sup>2</sup>	
	CaO	
	MgO	
	K <sub>2</sub> O	
	$\Lambda_2 \cup$	0.01
	Na <sub>2</sub> O	0.27
	H <sub>2</sub> Ô	2.48
	CuO	0.13
	PbO	
	(T) . ( . 1	100.05
	Total	100.02

This analysis is of especial interest in showing that the South Mountain piedmontite is a connecting link between three recognized members of the epidote group. In the first place, the amount of cerium and other rare earths which it contains indicates a considerable admixture of the allanite or orthite molecule; while the presence of both manganous and manganic oxides gives this mineral a position intermediate between true piedmontite and the mangan-epidote of Flink. Copper occurs extensively in the rocks which carry the piedmontite.

Another locality for piedmontite filling veins in the rhyolite was found near the head of Miney Run below the Clermont Hotel. While similar to that on Pine Mountain, the mineral is here less abundant.

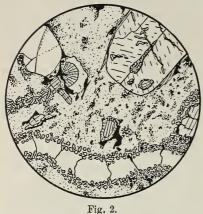
3. Piedmontite as a microscopic constituent of the rhyolite. —Although piedmontite has as yet been observed in macroscopic quantities in the South Mountain rhyolite only at the three localities above mentioned, it is quite generally disseminated as a microscopic constituent. Other occurrences like those already described will doubtless come to light as the detailed examination of the rhyolite area proceeds.

The reddest rhyolites contain microscopic piedmontite most abundantly and this color, as in the case of the well-known "porfido rosso antico," seems to be due to the mineral. The most representative specimens of this variety are from the small area of rather coarse and porphyritic rhyolite occurring just at Monterey station, Pa. This rock, which may be regarded as a type of all the others of this region like it, has a micropoikilitic\* groundmass enclosing good-sized phenocrysts of checkered anorthoclase and smaller ones of rounded quartz. It shows no particular evidence of dynamic action, though there is some secondary quartz and sericite present. The groundmass is full of black specks, probably manganese oxide resulting from the alteration of piedmontite, while there is every indication that the latter mineral, along with its associated rose and common epidote, is itself always of secondary origin. It occurs in veins or cracks in the feldspar phenocrysts and groundmass or in isolated patches, usually in association with secondary quartz, epidote and black manganese oxide. The piedmontite is not infrequently surrounded by a zone of pale rose or colorless epidote, which, however, seems to be rather granular than of continuous crystalline structure with the deep red mineral in the center (fig. 2).

As the microscopic piedmontite agrees in all its physical properties with the macroscopic, except for its greater tendency to mix in all proportions with the epidote molecule, no

\* G. H. Williams: "On the use of the terms poikilitic and micropoikilitic in petrography;" Journal of Geology, vol. i. p. 176, 1893.

attempt was made to isolate it. There is no reason to believe that it is not the same mineral as that concentrated in the veins.



Occurrence of microscopic p'edmontite in minute veins with secondary quartz and surrounded by rims of epidote. Magnified  $\times 25.$ 

As piedmontite is constantly increasing in importance as a rock constituent, it has appeared to the writer worth while to record all occurrences heretofore published. As far as possible he has made a comparative study of these occurrences.\*

We notice in epidote a tendency to form red varieties, just as, in the case of hornblende, there is a tendency to form blue ones (glaucophane, riebeckite, gastaldite, crocidolite). Thulite is red zoisite. The red epidote of Rotherkopf in the Tyrol<sup>+</sup> and the withamite of Glencoe in Scotland contain

very little manganese, and are comparable with the rose epidotes associated with the microscopic piedmontite of South Mountain and Japan.<sup>‡</sup> The recorded piedmontite occurrences which the writer has been able to find are as follows :§

1. With manganese ore deposits .- San Marcel,\* Viù, and Mezzenile, Italy (piedmontite); Jakobsberg,\* Sweden (mangan-epidote, with MnO only).

2. Spherulitic aggregates as veins in eruptive rocks. -Glencoe,\* Scotland\*\* (withamite); South Mountain,\* Penn.

3. Secondary constituent of eruptive rocks.—" Porfido rosso antico," Djebel Dokhan,\* Egypt++; Quartz porphyries of Missouri;\* ‡‡ granulite of Haute-Loire, France;§§ South Moun-tain,\* Penn.

\* For assistance in gathering material for this study the writer would express his gratitude to Mr. C. S. Bement of Philadelphia; Mr. J. S. Diller of Washing-ton; Prof. L. V. Pirsson of New Haven; Prof. B. Koto of Tokyo; Prof. G. Flink of Stockholm and Prof. A. Lacroix of Paris.

H. Bücking: Zeitschr. f. Kryst., vol. ii, p. 384, 1878.
 B. Koto: Jour. Coll. Sci., Imp. Univ. Japan, vol. i, p. 310, 1887.

\$ Asterisk denotes specimens studied by this writer.

Laspeyres: Zeitschr. f. Kryst., vol. iv, p. 435, 1880; Jervis, quoted by Hintze: Handb. Min., p. 255, 1890.

G. Flink: Zeitschr. f. Kryst., vol. xv, p. 88, 1889.
 \*\* D. Brewster: New Edinb. Journ. Sci., vol. ii, p. 218, 1825; Heddle: Min. Mag., vol. v, p. 15, 1882; Lacroix: Bull. Soc Min. de Fr., vol. vi, p. 75, 1886.
 † H. Rosenbusch: Die mass. Gest., 1st ed., p. 290, 1877; 2d ed., p. 472, 1887;
 Th. Liebisch, Zoitschr, d. geol. Goc. and and an analysis and 1877.

Th. Liebisch: Zeitschr. d. geol. Ges., vol. xxix, p. 717, 1877.

‡‡ E. Haworth: Inaug. Dissertation, Am. Geologist, vol. 1, §§ Lacroix: Minéralogie de la France, vol. i, p. 155, 1893. t E. Haworth: Inaug. Dissertation, Am. Geologist, vol. i, p. 365, 1888.

4. In crystalline-schists.—Chlorite sericite gneiss and glaucophane schist, Japan;\* on ilmenite from mica-schist, Island Groix, France;† in gabbro-diorite (alteration product of hornblende), Chichibu, Japan.‡

The writer is indebted to Messrs. Diller and Pirsson for two occurrences of piedmontite in quartz-porphyry which have not as yet been described. The first is in the porphyries and felsites of the Boston basin. Although Mr. Diller does not mention this mineral in his paper on these rocks, it occurs in at least six sections which were kindly loaned the writer for examination. From Mr. Pirsson the writer has a section of a porphyry almost identical with the common South Mountain type, which comes from the "Archæan area of Georgia near Tennessee." It has a finely developed micropoikilitic groundmass, considerable rather pale piedmontite (perhaps withamite), and is especially interesting as showing the persistence of the rhyolite to the southern end of the Appalachian region.

Petrographical Laboratory, Johns Hopkins University, Baltimore, March 24, 1893.

#### ART. VIII.—The Cambrian and the Ozark Series; by G. C. BROADHEAD.

In the Missouri Geological Report, 1873-74, the writer announced the finding of *Lingulella Lamborni* Mk. in the lower Magnesian limestone beds of Madison County and from that evidence the beds were referred to the age of the Potsdam. I have also obtained from the same beds a *Scolithus* and *Obolella polita*.

In various papers published by C. D. Walcott notably in this Journal for December, 1884, and in Bulletin 81 of the U. S. Geol. Survey—Correlation papers—Cambrian he has referred the Potsdam group to the age of the Upper Cambrian.

In an article by the writer of this paper read before the Am. Assoc. Adv. of Science, Cleveland meeting, 1888, and published in the American Geologist, January, 1889, entitled "The Geological History of the Ozark Uplift," the rocks of the Ozarks were defined and I made the statement that the Magnesian Series of the Ozarks were equivalent to the Upper Cambrian of C. D. Walcott. In a subsequent article published in the American Geologist for July, 1891, entitled the "Ozark Series" I have briefly described the several members of the

<sup>\*</sup> B. Koto: Jour. Coll. Sci., Imp. Univ. Japan, vol. i. p. 303, 1887.

<sup>+</sup> Lacroix : Bull. Soc. fr. de Min., vol. xi, p. 148, 1888.

<sup>‡</sup> T. Harada: Die Japanischen Inseln, Erste Lief. Berlin, 1890, p. 75.

series and stated that the second Magnesian limestone and the other series below to the Archæan seem to correspond with the description and position of beds referred by Mr. Walcott to the Upper Cambrian. I now make the additional statement that there is a similarity in character and composition of the entire series from the top of the first Magnesian to the lowest member of the Ozark series so as to make it seem proper to class the various members in one series the "Ozark Series."

The author of the article on the Cambrian and Ozark Series published in this Journal for March, 1893, would make us believe that he was the first person who had suggested the appropriateness of assigning this series to the age of the Cambrian, but as I have above stated the Cambrian age had been suggested before. Again, referring to Bulletin, No. 81, Correlation papers, Cambrian, Mr. Walcott says that "The Cambrian rocks occur in the southeastern portion of the State, about the Ozark Uplift. In several other places in the same Bulletin the Cambrian and Potsdam of Missouri are referred to. In the article above referred to, published in this Journal for March, 1893, a statement is made on pages 221 and 222 that in view of the recent work of the Missouri Geological Survey a new classification would be necessary. If necessary, it would be either for correction of former work done, or else on account of new discoveries. I do not consider that previous or present facts can justify any particular change.

Prof. Swallow defined the Magnesian limestone series (Ozark Series) and gave names to the principal beds in their order thus:

> First Magnesian limestone. First or Saccharoidal sandstone. Second Magnesian limestone. Second sandstone. Third Magnesian limestone. Third sandstone. Fourth Magnesian limestone.

The original section is in the main correct. Still there are certain beds found in one part of the State that cannot be entirely differentiated at other localities and some beds found at one place may be wanting at other places. Prof. Swallow recognized a third and a fourth Magnesian limestone on the Osage. The formation known as the Third Magnesian limestone includes certain beds which cannot be distinguished from the fourth Magnesian and it may be that the lower limestones of Madison County are of the age of the fourth Magnesian; if so, the two are not separated by a sandstone in Southeast

Missouri. On the Missouri River I have observed at several places lenticular beds of sandstones intercalated in the Second Magnesian and these sandstones sometimes may be traced for several miles, or as much as 15 miles.

In the well bored at the Insane Asylum, St. Louis, we find the following series :

Total depth.

1.	Loess to	40.	feet.
2.	Coalmeasures to	120	66
3.	Lower Carboniferous	883	66
4.	Lower Silurian	1304	66
5.	First Magnesian limestone	1452	"
6.	First sandstone	1585	
7.	Second Magnesian limestone "	2102	66
8. zi	Second sandstone	2184	66
Series.	Magnesian limestone, very cherty "	2671	66
	Magnesian limestone and sandstone. "	2843	66
11. 0zark	Sandstone	2880	66
12. Ö	Limestone	3022	66
13.	Sandstone	3120	66
14.	Magnesian limestone	3504	66
15.	Sandstone	3545	"
16.	Sandstone and limestone	3555	66
17.	Sandstone, there may be granite at base,	3843	"

This section indicates other sandstones besides the 1st, 2d They may be local beds. My general section in and 3d. Madison County is as follows:

	Chert beds		
2.	Magnesian limestone with chert and quartz.	100	"
3.	Magnesian limestone	125	66
	Gritstone and Lingula beds		
	Marble beds 5 t		
6.	Sandstone and conglomerate 5 t	o 90	"

Near the Iron Mountain, Conglomerate rests on the Porphyry; eastwardly on St. François River in Madison County the lower beds of the sandstone are pebbly and rest upon granite. Near Fredericktown the series appears thus:

- 1. Magnesian limestone.
- 2. Gritstone.
- 3. Sandstone.
- 4. Red Slatv sandstone.
- 5. Granite.

Ten miles west, No. 4, of this section is over 20 feet thick, with layers of sandstone and conglomerate above.

In the northern part of Madison County the marble beds are wanting, but the gritstone beds are present. In the southern

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portion of the county we find both. On west side of St. François River not far from mouth of Leatherwood Creek the section shows :

1-4 feet Magnesian limestone.

2-4 feet Gritstone.

3–9 feet of Magnesian limestone.

4-3 feet of Gritstone.

5-11 feet of Magnesian limestone.

6-20 feet of Marble beds.

On Twelve Creek I have found the Gritstone beds resting on the marble which in turn rests upon the porphyry. In this way I obtained my general section of Madison County as above. On Marble Creek in Iron County the Magnesian limestones are seen resting directly upon the porphyry.

The sandstone and the Marble beds not being persistent are found at some places resting upon the porphyry or granite (Archæan) at other places the limestones rest directly upon the Archæan. The upper beds of the Ozark Series are in the main persistent. Near Augusta the regular succession, from first Magnesian to second Magnesian is preserved. At Crystal City, Pacific and Westpoint, Ill., the two upper members are well exposed. On the Gasconade and Osage the second and third Magnesian limestones with the separating and incumbent sandstones are well marked. So, taking all the evidence in the case one had better go very slow before he attempts a new arrangement or classification.

#### ART. IX. — A One-Volt Standard Cell; by HENRY S. CARHART.

[Read before the National Academy of Sciences, Washington, April 21, 1893.]

THE calomel cell, consisting of mercury in contact with mercurous chloride and zinc in a solution of zinc chloride, was first described by von Helmholtz in 1882.\* Without any knowledge of its previous invention I made the same cell six years ago and have still the first sample made at that time. Ostwald + refers to a calomel cell giving one volt E. M. F. at 15° C., the density of the zinc chloride being 1.409 at 15°, and the temperature coefficient +.00007 volt per degree.

Within the last few months I have taken up the calomel cell again with a view of adjusting it to precisely one volt, making a careful determination of its temperature coefficient, and investigating its reliability.

> \* Sitzber. der Akad. der Wiss., p. 26, Berlin, 1882. † Zeitschrift für Physikalische Chemie, vol. i, p. 403.

It is now well known that the E. M. F. of a voltaic cell with zinc immersed in a solution of one of its salts decreases with increase of density of the solution.<sup>\*</sup> Within limits therefore the E. M. F. of a cell can be varied by changing the density of the solution of the zinc salt. Thus the E. M. F. of a Clark cell was found to vary from 1.434 volts with a solution saturated at 20° C. to 1.481 volts with a 5 per cent solution, a variation of nearly three and one-third per cent.

The variation of the E. M. F. with density is even greater in the case of zinc chloride. With zinc chloride 16 per cent increase of density produces 3 5 per cent decrease in E. M. F. An equal increase of density of zinc sulphate is accompanied by only half the percentage decrease of E. M. F. Hence greater care is necessary in standardizing a solution of zinc chloride than of zinc sulphate.

Taking the Clark cell with excess of crystals of zinc sulphate as the standard, having an E. M. F. of 1.434 volts,  $\dagger$  at  $15^{\circ}$  C., I have found that the density of the zinc chloride solution required to give one volt is 1.391 at  $15^{\circ}$  C. Ostwald's density gives too low a value. It was probably adjusted to correspond with the legal ohm.

The cell is made in the same form as my Clark standard. In the bottom of the tube is pure mercury in contact with a platinum wire; on this a paste of mercurous chloride and the zinc chloride solution; a cork diaphragm follows, holding the mercury and paste firmly in position, especially with some asbestos packing under the cork; zinc chloride is then added to the proper depth, and an amalgamated zinc rod, supported by a cork, completes the electrical combination of parts. The cell must be hermetically sealed as usual. Such a cell is perfectly portable and gives promise of long life. Its internal resistance is about 1500 ohms, and it does not appear to suffer permanent change by heating to 50° C. or even to 60°. The cell six years old already mentioned is still in good condition and has apparently maintained its E. M. F.

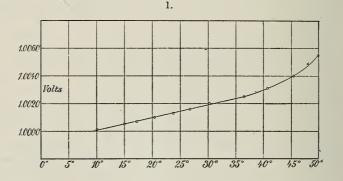
An interesting feature of this cell is its small positive temperature coefficient. It is well known that the coefficient of the Clark and the Daniell standard is negative. The calomel cell has a coefficient of about +.00009 within working limits of temperature. In the following table will be found the data of one series of observations on the temperature coefficient :

<sup>\*</sup> Carhart, this Journal. Nov. 1884, p. 374.

<sup>†</sup> Report of the B. A. Committee, Edinburgh Meeting, 1892.

		TABLE I.		
No.	30. Clark.		No. 8.	$ZnCl_2$
Resistance		Resistance		Electromotive
to balance.	Temp. C.	to balance.	Temp. C.	force in volts.
9401	$18^{\circ}.25$	6572	13°•7	1.0000
		6608	48.9	1.0055
		6604	48.0	1.0049
		6598	45.4	1.0040
		6592	40.7	1.0031
		6589	36.4	1.0025
9402 +	18°·25	6586	30.2	1.0020
		6583	26.7	1.0016
		6581	23.7	1.0013
		6579	20.4	1.0010
		6577	17.2	1.0007
		6576	15.0	1.0002
9403	18°•1	6573.5	10.0	1.0001

The E. M. F. of the Clark is taken as 1.434 at  $15^{\circ}$ ; temperature coefficient -.00077. It will be observed that the cell does not recover its normal E. M. F. immediately on descending temperatures. This hysteresis phenomenon however is small, amounting only to an error equivalent to about three degrees of temperature. The entire change of temperature of about  $40^{\circ}$  took place within three hours. The observations of the table are plotted in the curve of fig. 1. The curve is approximately a straight line between ten and forty degrees. Beyond



this point the coefficient increases rapidly. The equation of the curve contains not only a quadratic term but one which is a function of a still higher power of the temperature. The following equation fits the observations fairly well:

 $\mathbf{E}_{t} = 1 + \cdot 000085(t-15) + \cdot 0000006(t-15)^{2} + \cdot 00000001(t-15)^{3}.$ 

Between ten and thirty degrees the relation between E. M. F. and temperature may be expressed as follows:

 $E_t = 1 + .000094(t - 15).$ 

The coefficient is therefore a little less than  $\frac{1}{7 \cdot b}$  per cent per degree. A neglected variation of temperature of 10° C. can cause an error of only  $\frac{1}{7 \cdot b}$  per cent. In another paper\* I have given an analysis of the tempera-

In another paper<sup>\*</sup> I have given an analysis of the temperature coefficient of both the Clark and the Daniell cell when the former contains no excess of zinc sulphate crystals, and have shown that this coefficient is a purely thermo-electric phenomenon at the contact of a metal and a liquid. Further investigations confirm this conclusion that the temperature coefficient of a voltaic cell is the result of the superposition of the two thermoelectromotive forces of the metal and the salt in contact with it on the two sides of the cell, whenever this coefficient is not complicated with oxidation effects and the solution and recrystallization of salts. In the old Clark cell almost exactly half the temperature coefficient is due to changes in density of the solution by reason of the presence of an excess of zinc sulphate crystals.

These dissolve when the temperature rises and again slowly crystallize out on a falling temperature. Time is required for diffusion, and the cell is therefore slow in reaching its electrical equilibrium after a temperature change. This time lag may extend over several days. It is very appreciable when the temperature change does not exceed one degree an hour.

Whether a resultant temperature coefficient shall be positive or negative depends upon the relative values and the signs of the two thermo-electromotive forces at the two sides of the couple. To measure these electromotive forces of thermal origin I have made use of an experimental cell consisting of two glass tubes 12<sup>cm</sup> long and 1<sup>cm</sup> to 2<sup>cm</sup> in diameter, joined near the top by a small tube 17<sup>cm</sup> long, having near the middle a narrow bore made by thickening the walls of the tube. When it is desirable to use two liquids a plug of asbestos is placed at the narrow part of the connecting tube to aid in filling without admixture of the liquids and to diminish diffusion. When the thermo-E. M. F. between a metal and a liquid is to be determined the experimental cell is filled with the liquid and wires of the same metal, cut from one piece, are inserted in the two limbs. One limb is then kept in melting ice and the other is raised to different temperatures, and the resulting E. M. F. measured. For this latter purpose the most exact method, giving practically an electrostatic measurement, is to balance the E. M. F. of a standard cell against the fall of potential over the requisite resistance in a circuit of constant high resistance (10,000 ohms), as in the Rayleigh or compensation method of comparing electromotive forces.<sup>†</sup> The experimental cell is then

\* London Electrician, June 12, 1891; Carhart's Primary Batteries, pp. 136-150. † Phil. Trans., Part II, 1884, p. 441. put in series with the standard cell, and the resistance in the shunt of the main circuit required to maintain a balance shows both the value and the direction of the E. M. F. of the experimental cell as compared with the standard.\*

By this method the mean thermo-E. M. F. of Cu-CuSO<sub>4</sub>---Cu per degree between 0° C. and 50° C. I have found to be +.00073 volt. The positive sign indicates that the metal in the warm solution is positive externally to the one in the cold, or the metal in the cold plays the part of the zinc of a voltaic couple. Bouty gives the E. M. F. of  $Fe - FeSO_4 - Fe$  as zero. It follows that a couple consisting of Fe - FeSO -CuSO<sub>4</sub>—Cu should have a positive temperature coefficient, and this coefficient should be the same whether the whole cell is heated or only the copper—copper sulphate side. Experiment confirms the first conclusion at least. The E. M. F. of the cell at 15° C. was found to be 0.625 volt, and at 29°.4 C., 0.637 The change is therefore +0.000833 volt per degree and volt. the coefficient is  $0.000833 \div 0.625 = 0.0013$ , or over  $\frac{1}{10}$  per cent.

Theoretically it should be

#### $0.00073 \div 0.625 = 0.0012$ .

The above combination is now used as an iron gravity battery, and the change in its E. M. F. with a sudden change of the temperature of the room had attracted my attention before I had investigated the temperature coefficient. After the above iron-copper cell had been left standing for twenty-four hours, with a piece of iron wire in the connecting tube of the experimental cell to intercept the CuSO<sub>4</sub> which might diffuse over, the E. M. F. was found to be 0.651 volt at 14°.4 C.; and for a range of 7.7 degrees the temperature coefficient was 0.0012. This is exactly the value obtained from theoretical considerations.

Another case in point is that of the voltaic series

#### $Ni-NiSO_4-CuSO_4-Cu.$

The E. M. F. was quite variable and only an approximate measurement could be made. The temperature coefficient was positive and equal to 0 0084, or over  $\frac{8}{10}$  per cent per degree C. The actual change in E. M. F. was greater than this, for the E. M. F. continued to fall on standing and the change by heating was thus in part masked.

The thermal-E. M. F. of copper—copper sulphate is positive, while that of nickel—nickel sulphate is negative. Hence the temperature coefficient of the above series should be positive and equal to the sum of the two thermal E. M. F.'s. The result is positive but not equal to the sum of the two thermal

\* Carhart's Primary Batteries, p. 137. + Journal de Physique, vol. ix, p. 229.

E. M. F. values. Perhaps no closer numerical agreement could be expected in the case of a variable E. M. F.

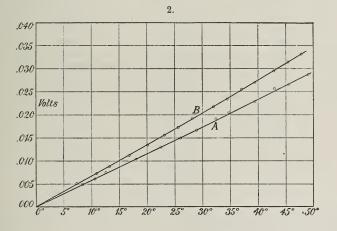
In the light of the above conclusions and with thermo-electric data furnished by Bouty and by Chroustchoff and Sitnikoff\* it is easy to draw the conclusion that the temperature coefficient of the calomel cell should be negative and of small value. The thermo-E. M. F. or value of  $\frac{dE}{dT}$  for Zn - ZnCl<sub>2</sub>-Zn is given by Bouty as 0.000696; Chroustchoff and Sitnikoff found that of Hg-Hg<sub>2</sub>Cl<sub>2</sub>-ZnCl<sub>2</sub>-Hg<sub>2</sub>Cl<sub>2</sub>-Hg to be 0.00066 between 0° and 50° C.

Hence the coefficient should be,

0.00066 - 0.000696 = -0.000036.

The value of  $\frac{dE}{dT}$  for zinc in zinc salts given by Chroustchoff and Sitnikoff would give a larger negative coefficient than the above.

I have therefore investigated this subject to ascertain if this case furnishes an exception to the law of temperature coeffi-



cients already announced. The result confirms the law and shows Bouty's result to be in error The determinations were made by means of the experimental cell in the manner already indicated. Tables II and III contain the observations which are expressed graphically in the two curves of fig. 2, in which

A. relates to 
$$Zn - ZnCl_2 - Zn$$
, Table II, and

B. to Hg-Hg<sub>2</sub>Cl<sub>2</sub>-ZnCl<sub>2</sub>-Hg<sub>2</sub>Cl<sub>2</sub>-Hg, Table III.

\* Comptes Rendus, vol. cviii, 1889, p. 937.

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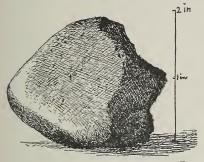
	TABLE II.	
Difference of	Total E. M. F.	
Temperature.	in volts.	E. M. F. per degree C.
49°•0	$\cdot 02876$	.000587
45.5	$\cdot 02662$	$\cdot 000585$
42.9	$\cdot 02570$	·000579
39.4	$\cdot 02295$	.000582
34.8	$\cdot 02050$	•000589
32.4	·01913	$\cdot 000590$
28.9	*01668	.000577
26.1	·01499	000574
22.5	.01301	.000578
18.0	$\cdot 01040$	·000580
12.6	.00750	·000595
10.6	.00612	.000577
8.4	.00490	.000583
	Mean,	+.000584
	TABLE III.	
Difference of	Total E. M. F.	
Temperature.	in volts.	E. M. F. per degree C.
$47^{\circ} \cdot 8$	·03314	.000693
45.4	.03146	.000693
42.8	$\cdot 02949$	.000689
39.4	$\cdot 02706$	.000686
37.1	$\cdot 02554$	.000688
34.4	.02340	.000680
32.1	.02174	.000677
28.2	.01928	.000687
25.6	$\cdot 01729$	$\cdot 000675$
23.1	.01561	$\cdot 000675$
20.1	.01353	$\cdot 000673$
16.8	.01125	.000669
13.2	.00882	.000668
10.9	.00730	.000669
7.4	.00517	.000698
	Mean,	+.000681

Both of these thermal E. M. F.'s are positive. The temperature coefficient should therefore be

0.000681 - 0.000584 = 0.000097 as a mean.

This corresponds very closely indeed with the value found by observation on a one-volt cell. It will be observed that it is only necessary to take the difference of the above electromotive forces to obtain the temperature coefficient, since the E. M. F. of the cell is one volt. The coefficient is positive because the value of  $\frac{dE}{dT}$  for the positive side of the cell is in excess of that for the negative side. ART. X.—Cross Roads Meteorite; by Edwin E. Howell.

LAST September I purchased from Mr. B. E. Barnes of Boyett, N. C. (who secured it of the finder about three weeks after it fell), a small aerolite which is here figured. It fell in the early morning about five o'clock, May 24th, 1892, in the township of Cross Roads, Wilson Co., N. C., and was seen by



a young man named Gray Bass, who was only about two hundred feet distant. He seems to have been frightened by the sight and sound and waited two or three hours before going to the spot. With a stick he then dug up the meteorite, which penetrated 4 or 5 inches into the packed but sodded earth close by a road bed. Young Bass

also states that some of the grass near the spot was dead and looked as if killed by fire! He further says that he thought the meteorite came from the northwest. From the testimony of others who heard it, however, it seems undoubtedly to have come from exactly the opposite direction, having been heard as far away as eighteen miles in a S. E. direction. Among those who heard it was a colored boy one quarter of a mile to the S. E., Mieajoh Hales, four to six miles to the S. E. who describes the noise as "somewhat like thunder accompanied by lesser sounds like the report of pistols or the snapping of burning reeds." Another man, Edward S. Dees, distant five or six miles nearly south, wrote in answer to my inquiries, that one clear morning before sunrise sometime in May he was in the open field and heard a peculiar noise which lasted a quarter of a minute and sounded like "a freight train crossing a trellis"thought it came from the S. W. Wm. B. Scott, about eighteen miles to the S. E., writes that before sunrise on the 24th of May he and a neighbor heard a noise "something like a sky rocket but more like thunder which went off in a northern direction."

Mr. Barnes sent the stone first to the National Museum and a fragment weighing  $4\frac{1}{2}$  grams was broken off. With the exception of this piece nothing has been taken from it since it was picked up; several small chips however were broken off before it reached the ground and the broken surface partly crusted again. It now weighs 157 grams and it would probably have weighed about 200 grams, if it had reached the earth unbroken.

The thick even crust coating the meteorite indicates that it was a complete individual and not one of a shower. The freshly broken surface is of the usual gray color and the structure is chondritic. The dimensions of the stone are 1, 2 and  $2\frac{1}{2}$ inches. The specific gravity is 3.67, which is somewhat greater than most meteorites of this class, indicating a little more iron.

Washington, June 13, 1893.

#### SCIENTIFIC INTELLIGENCE.

#### I. CHEMISTRY AND PHYSICS.

1. On the Study of Chemical Reactions by means of the Refractive Index.-It has been shown by FERY that the occurrence of chemical changes in solution may be detected and studied, by comparing the refractive indices of solutions containing two substances which are capable of acting one on the other, with those calculated on the assumption that the observed index is the mean of the indices of the two constituents. In a solution containing sodium hydroxide and nitric acid for example it was observed that the maximum deviation of the experimental from the calculated values occurred in a solution containing 8 parts of NaOH and 12.31 parts of HNO<sub>3</sub> in 100 of water, the ratio 12.31/8.00 being nearly equal to that of HNO<sub>3</sub>/NaOH. When alkalies are mixed with sulphuric acid, there are two points at which changes of the refractive index occur in the curve, one corresponding with a mixture that would form an acid salt, the other to one that would form the normal salt. In the case of phosphoric acid the curve has three such points. In cases where no chemical action occurs, the observed and calculated values for the indices of refraction are found to coincide, the curve for the refractive indices of such mixtures being a continuous straight line. Moreover, the author has observed certain other slight breaks and changes in the refractive-index curve, which he attributes to the formation of special hydrates by the union of water with the substances under examination. In the case of sulphuric acid, a special study showed that such breaks occurred with solutions corresponding to hydrates of  $H_2SO_4$  with one, one and a half, two and four molecules of water respectively .- C. R., cxv, 1309; J. Chem. Soc., lxiv, ii, 201, May, 1893. G. F. B.

2. On the Preparation of Chlorine by means of Nitric Acid and Manganese dioxide.—Several years ago Schlösing proposed a process for preparing chlorine by acting on hydrochloric acid with manganese dioxide and nitric acid; the reaction taking place according to the equation:

#### $MnO_{2} + (HCl)_{2} + (HNO_{3})_{2} = Mn(NO_{3})_{2} + (H_{2}O)_{2} + Cl_{2}$

and evolving theoretically the whole of the chlorine contained in the hydrogen chloride. In practice, using the dioxide and the hydrochloric acid (sp. gr. 1.184) in the proportion given in the equation, and nitric acid (sp. gr. 1.4245) in excess to the extent of 75 per cent, a yield of 98–99 per cent of the calculated quantity of chlorine is obtained. To the acid mixture one-seventh of its volume of water is added and the whole is heated to 135°. LUNGE and PRET have studied this reaction more completely. They find that the resulting manganese nitrate may be entirely converted, by heating, into manganese dioxide and the lower oxides of nitrogen; the reaction beginning somewhat suddenly and vigorously, about  $180^{\circ}-190^{\circ}$  and being completed at  $250^{\circ}$  in a proportionately shorter time. The evolved nitrogen oxides, by mixture with air and conduction into water are re-converted into nitric acid. But this regeneration is never complete; even when conducted at the ordinary temperature or in fact at a lower one. Moreover, since there is also a loss of nitric acid during the evolution of the chlorine—though in what form is doubtful, a portion probably escaping as nitrosyl chloride—the authors conclude that owing to this considerable loss of nitric acid, amounting at least to 10 per cent and perhaps to 16 per cent of the acid used, the chlorine method of Schlösing, commercially, has material disadvantages.—*Ber. Berl. Chem. Ges.*, (Ref.) xxvi, 309, May, 1893. G. F. B.

3. On Complex Acids containing Septivalent Iodine.—BLOM-STRAND has described certain complex inorganic acids containing the quinquivalent group IO of periodic acid, analogous to the trivalent group PO in phosphoric acid. These acids are classed as monomolybdoperiodic acid  $IO(OH)_4$ . O. MoO<sub>2</sub>. OH, tetra-molybdoperiodic acid  $.IO(OH)_3(O. MoO_2. O. MoO_2. OH)_4$  and  $.IO(OH)_3(O. MoO_2. O. MoO_3. OH)_4$  and  $.IO(OH)_3(OH)_3(OH)_4$  and  $.IO(OH)_4(OH)_4$  and  $.IO(OH)_4(OH)_4(OH)_4(OH)_4$  and  $.IO(OH)_4(OH)_$ hexamolybdoperiodic acid IO(OH), (O. MoO2. O. MoO2. OH); The hexamolybdoperiodates were prepared by heating periodic acid or the corresponding periodate with molybdic acid and the carbonate of the same metal, in aqueous solution, until the whole had dissolved, and then allowing crystallization to take place spontaneously. In some cases a dilute solution of the acid itself was prepared from a mixture of periodic acid and barium molybdate by adding sulphuric acid, and this solution was then neutralized by a metallic carbonate. The acid solution on evaporation yielded a transparent amorphous mass with no trace of crystallization. The sodium salt crystallizes with  $(H_2O)_{17}$  in rhombohedrons, and with  $(H_2O)_{18}$  in triclinic prisms; the hydrogen potassium salt crystallizes with  $(H_2O)_{12}$  in four or six sided triclinic plates; and the little in the little in the little in the little set of the litt the lithium salt Li<sub>5</sub>Mo<sub>6</sub>IO<sub>24</sub>(H<sub>2</sub>O)<sub>15</sub> crystallizes in rhombohedrons. The ammonium and the calcium salts, and also double salts of strontium-sodium, barium-sodium and manganese-sodium are described. By treating the ammonium salt of the hexa-acid with ammonia, the tetramolybdoperiodate is obtained; and by treating the sodium salt similarly, ammonium-sodium monomolybdoperiodate is prepared crystallizing in quadrangular triclinic plates containing four molecules of water.-Zeitschr. anorg. Chem. i, 10; J. Chem. Soc., lxiv, (ii), 122, March, 1893. G. F. B.

4. On the Refractive Indices of liquid Oxygen, Nitrogen Monoxide and Ethylene; and on the Spectrum of liquid Oxygen.— LIVEING and DEWAR have determined the constant of refraction  $(\mu_p-1)/d$  for oxygen at its boiling point  $-182^{\circ}$  and found it to be 0.1989, it refraction-equivalent at this temperature being 3.182. Using the formula  $(\mu^2-1)/(\mu^2+2)d$ , the corresponding values are 0.1265 and 2.024. Liquid nitrogen monoxide at  $-90^{\circ}$  gives for the value of  $(\mu_{\rm p}-1)/d$ , 0.2634, and for  $(\mu^2-1)/(\mu^2+2)d$ , 0.163; the molecular refraction-equivalents being 11:587 and 7:163 respectively. Ethylene at  $-100^{\circ}$  gives 0.627 for the value of  $(\mu_{\rm p}-1)/d$  and 0.384 for  $(\mu^2-1)/(\mu^2+2)d$ ; the corresponding numbers for gaseous ethylene being 0.578 and 0.385. By viewing the incandescent pole of the electric arc through a column of three inches of liquid oxygen, with a spectroscope having two calcite prisms of 30° and one of 60°, the red potassium lines being used as reference lines, the authors have obtained the absorption spectrum of this element. In place of the solar line A, a band was observed having a sharp edge on the less refrangible side and fading away gradually on the more refrangible side. The sharp edge did not coincide with the sharp edge of A, the wave length being about 7660. No band corresponding with B was observed but through a thickness of 6 inches of liquid oxygen a faint band appeared which had precisely the same character as A, the wave length of its sharp edge being 6905. Liquid oxygen is distinctly blue, this color, apparently not being due to ozone. Ozone at a low temperature explodes with great violence .- Phil. Mag., V, xxxiv, 205, March, 1893. G. F. B.

5. On the Production of Hydrogen Peroxide in the Electrolyis of Sulphuric acid.-KURILOFF has investigated the production of hydrogen peroxide and of persulphuric acid when dilute sulphuric acid of different strengths is electrolyzed. He employed for this purpose an apparatus which permitted the separate collection of the products formed at the two electrodes. The hydrogen peroxide was determined by titration with potassium permanganate and the persulphuric acid by adding a known quantity of ferrous salt to the solution and titrating back with potassium permanganate. The results of his experiments are: (1) The quantity of hydrogen peroxide formed is very small; (2) hydrogen peroxide and persulphuric acid may be simultaneously formed at both electrodes, but the peroxide is not always accompanied by persulphuric acid; (3) the formation of both products is intimately connected with the concentration. Persulphuric acid only appears when the solution contains over 1 per cent of sulphuric acid; hydrogen peroxide when the concentration is over one per cent; (4) mixtures containing 3, 47 and 73 per cent of acid respectively behave differently from other mixtures with regard to the amount of peroxide formed when they are electrolyzed. This is considered by the author to be due to the fact that the composition of these solutions approximates to that required by the hydrates containing  $(H_2O)_{150}$ ,  $(H_2O)_6$  and  $(H_2O)_2$  to each molecule of  $H_2SO_4$ , since according to Mendeléeff all these hydrates exist in solution.-J. Soc. Chim. Russe, xxiii, 235; J. Chem. Soc. London, lxiv, (ii), 108, March, 1893. G. F. B. 6. On the Preparation of Pure Phosphoric oxide.—As usu-

6. On the Preparation of Pure Phosphoric oxide.—As usually prepared, phosphoric oxide always contains more or less of the lower oxides mixed with it. SHENSTONE and BECK have proposed to obtain it pure, by passing it in vapor mixed with oxygen, over platinum sponge. For this purpose a piece of combustion-tube about 90cm long and 2cm in diameter, is divided into two nearly equal chambers by a constriction, a small lateral tube rising from the constricted portion. Immediately beyond this the tube is packed with fragments of platinum sponge; and on the other side of it is placed a large platinum boat containing the phosphoric oxide previously compressed into cylinders. The platinum sponge is heated to redness and a current of oxygen is supplied at the end of the tube and also at the middle by the lateral tube above mentioned. The sublimed product is received in a tube sliding into the combustion-tube near its end, from which it is pushed into a well dried bottle. As thus prepared, the phosphoric oxide no longer reduces a solution of silver-nitrate nor one of mercuric chloride. Nor does its solution on evapora-tion and ignition give the odor of phosphine. It doubtless contains a little metaphosphoric acid. The authors find that the last traces of the lower oxides are not removed by this roasting in oxygen even for weeks .- J. Chem. Soc., lxiii, 475, April, 1893. G. F. B.

7. On the Constitution of Hydroxylamine.—In view of the fact that hydroxyl compounds of nitrogen give up more or less readily the elements of water to form new nitrogen compounds, KOLOTOFF has sought by acting on hydroxylamine with ammonia to bring about the reaction  $NH_2$ .  $OH + NH_3 = N_2H_4 + H_2O$ . It was found, however, that this reaction did not take place even when the two substances were heated together at 100° for 24 hours. He therefore concludes that free hydroxylamine contains no hydroxyl and that its formula should be  $H_3N : O$ . Moreover, it is known that when a salt of hydroxylamine is treated with a solution of bromine in an excess of strong sodium hydroxide only half its nitrogen is evolved in the free state, the other half being probably oxidized to acid, according to the equation:

#### $(NH_{3}O)_{2} = NH_{3} + HNO + H_{2}O$

the ammonia itself being subsequently oxidized. To test this view the author oxidized in the cold a weighed quantity of a hydroxylamine salt, dissolved in a large excess of NaOH, with the theoretical quantity of bromine required by the above equation. After removal of the excess of soda the solution was precipitated with copper sulphate, the precipitate collected, dried and weighed. Its mass was  $4 \cdot 9^{\text{grms}}$  that required by theory being  $4 \cdot 3^{\text{grms}}$ ; corresponding to the formula  $\text{Cu(NO)}_2$ . H<sub>2</sub>O. It does not lose weight when heated to 136° but blackens when treated with soda. The author considers it to be the dihydrogen cupric salt of an acid H<sub>4</sub>N<sub>2</sub>O<sub>3</sub> which he calls "pyrohyponitrous acid." Hydroxylamine sulphate loses weight at  $125^{\circ}-130^{\circ}$ , very rapidly at  $136^{\circ}$ , the maximum loss being  $28 \cdot 4$  per cent. The ratio between the nitrogen and sulphur in the residue seems to suggest formation of salts of both N<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>H<sub>2</sub>·—J. Soc. Chim. Russe, xxiii, 3; J. Chem. Soc. London, lxiv, (ii), 114, March, 1893.

G. F. B.

8. Chromophotography.—M. MAREY, continuing his studies upon the application of instantaneous photography to the investigation of the motion of swimming animals, has devised a special form of apparatus which he believes will prove of great utility in experimental hydrodynamics. A tank is filled with water in which is suspended a number of small bodies consisting of a mixture of wax and rosin which are silvered. The density of the water is then suitably modified by the addition of salt or other substance, in order that the small bodies may be disseminated throughout the liquid. The side of the tank has a backing of black velvet and light is reflected into the water by means of suitably placed mirrors thus illuminating the suspended particles. Interesting reproductions of photographs are given.—Comptes Rendus, May 1, 1893, pp. 913–924. J. T.

9. Reflection of Electrical Waves at the extremity of a linear Conductor.—Mr. BIRKELAND points out the applicability of Poynting's theories for the explanation of the resonance phenomena discovered by Hertz. The electromagnetic energy in the field surrounding the conductor moves in space in a direction normal to the lines of electric force and magnetic force at each point. By considering this theorem, Birkeland is led to an explanation of multiple resonance, and to the various discrepancies between theory and experiment noticed by those who have studied the Hertz phenomena.— Comptes Rendus, April 17, 1893, pp. 803–806. J. T.

10. Electrical Waves and light waves.—V. BJERKNES finds that the extinction power of metals for electrical waves increases with good conductors. It also increases with the magnetism of the conductor. The swifter the electrical waves the less distance do they penetrate into the conductor. The author points out various discrepancies between the electromagnetic theory of light, the ordinary theory, and believes that electrical waves represent the motion of molecules as a whole, while the ordinary light waves deal with the motion of individual molecules. He also believes that a study of the action of very quick electrical oscillations on magnetic molecules will fix a limit to the inertia ratio of an iron molecule.—Ann. der Physik und Chemie, No. 4, 1893, pp. 592– 605. J. T.

11. New Electrometers.—BJERKNES has described a new electrometer which he has used in his researches on Hertz phenomena; it consists of a thin plate of aluminum suspended at an angle of 45° between thin plates of an air condenser. When the latter are connected with the poles of a Ruhmkorf coil the aluminum plate tends to set in the line of electrical force between the plates. A simple formula connects the angle of turn of the plate with the difference of potential of the terminals or plates of the air condensers. C. Christiansen suspends two plates separated by mica, by suitable wire, between the plates of an air condenser. When the latter are maintained as a certain difference of potential, the suspended plates tend to turn so as to place themselves at right angles to the lines of force between the condenser plates. The author gives the simple theory and examples of the working of the new instrument.—Ann. der Physik und Chemie, No. 4, 1893, pp. 592-605, pp. 726-733. J. T.

12. Magnetic Properties of Liquid Oxygen .- At a discourse delivered before the Royal Institution, Professor Dewar exhibited a pint of liquid oxygen. The temperature of the liquid oxygen at atmospheric pressure was 180° C. Reference was made to a remarkable experimental corroboration of Lord Kelvin and Professor Tait's thermo-electric diagram for low temperatures. If lines of copper and platinum were prolonged in the direction of negative temperature they should intersect at -95° C. Similarly copper and palladium lines would cut one another at  $-170^{\circ}$  C. If the diagram is correct the E. M. F. of the thermo-electric junction of these pairs of metals should reverse at these points. A Cu-Pt junction connected to a reflecting galvanometer was placed in oxygen vapor and cooled down. At  $-100^{\circ}$  C, the spot of light stopped and reversed. A Cu-Pd junction placed in a tube containing liquid oxygen gave a reversal at  $-170^{\circ}$  C. Liquid oxygen is a non-conductor of electricity. A spark taken from an induction coil one millimeter long in the liquid requires a potential equal to a striking distance in air of 25<sup>mm</sup>. Thus oxygen is a high insu-The magnetic moment of liquid oxygen is about 1000, lator. when the magnetic moment of iron is taken as 1,000,000. Between the poles of the magnet all the liquefied air went to the poles, there was no separation of the oxygen and nitrogen. Liquid air has the same high insulating power as liquid oxygen. At -200° C. the molecules of oxygen had only one-half of their ordinary velocity, and had lost three-fourths of their energy. Liquid oxygen had no action upon a piece of phosphorus and potassium or, sodium dropped into it. A photographic plate placed in liquid oxygen could be acted upon by radiant energy and at a temperature of -200° C. was still sensitive to light. Professor M'Kendrick had tried the effect of low temperatures upon the spores of microbic organisms by submitting in sealed glass tubes blood, milk, flesh, and similiar substances for one hour at a temperature of  $-182^{\circ}$  C. and subsequently to a temperature of blood heat. The tubes on being opened were all putrid. Seeds also withstood a similar amount of cold. These experiments proved the possibility of Lord Kelvin's suggestion that life may have been brought to the newly cooled earth upon a seed-bearing meteorite.-Nature, May 25, 1893, pp. 89-91. J. T.

13. Specific Heat of Liquid Ammonia.—Dr. Hans von Strombeck has called the attention of the editors to the paper by himself in volume cxxx of the Journal of the Franklin Institute (Dec. 1890, p. 467) in which he gives a detailed account of his determination of the specific heat of liquid ammonia. The mean result obtained was 1.22876. This result should properly have been referred to in the paper upon the same subject published in our March number of this year, page 200. 14. On the value of the meter in English inches; by C. B. COMSTOCK, U. S. A. (Communicated).—In April 1885 I read a paper before the National Academy of Sciences in which the value of the meter in terms of the yard was given, as derived from comparisons of a meter (R 1876) and Clarke yard A, both formerly belonging to the U. S. Lake Survey. This value was, meter = 39.3699 inches.

A note from Dr. Benoit of the International Bureau of Weights and Measures of 27 March 1893, gives the value of the Toise of Bessel in terms of the meter, from Dr. Benoit's comparisons: of Toise No. 10 in terms of the Toise of Bessel from Peter's comparisons and of Toise No. 10 in terms of the yard from Clarke's comparisons: the resulting value of the meter is,

#### Meter=39.3699 inches.

These equal results obtained through independent routes, indicate that this value has a high degree of accuracy.

Army Building, New York City,

May 17, 1893.

15. A Student's Manual of a Laboratory Course in Physical Measurements; by WALLACE CLEMENT SABINE. 126 pp. Boston, 1893. (Ginn & Co.).—This little manual is of special interest as detailing the series of 72 experiments given in the prominent Physics course at Cambridge as also at the Harvard summer school. As given in the college, it requires about 180 hours from the student in the laboratory with the requirement of one half as much time given to outside study.

#### II. GEOLOGY AND MINERALOGY.

1. The Tertiary Revolution in the Topography of the Pacific Coast; abstract of a paper read May 10th, 1893, by J. S. DILLER before the Geological Society of Washington, D. C. A preliminary study of the ancient plains and peneplains of erosion in Northern California and the distribution of the associated sedimentary formations laid down upon their borders, as well as of the large masses of the auriferous gravels deposited upon their gentle slopes, has thrown much light upon the condition of that region during the Eocene and early Neocene. It has afforded a basis for estimating the amount of elevation which the northern end of the Sierra Nevada has experienced since the close of the Miocene. In the Lassen Peak region strata which were laid down during the Miocene in an estuary have since been raised in one place to 3400 and in another to 4000 feet above the sea. The amount of elevation in that district increases southward and at the northern end of the Sierra Nevada the upheaval has been at least 4000 feet and probably over 5000 feet. The Klamath mountains and Coast range have been even more profoundly affected by the same movement.

2. On Urnatella gracilis; by C. B. DAVENPORT. Bulletin Mus. Comp. Zoöl., vol. xxiv, No. 1, pp. 1-44, plates 1-6, 1893.— This little known and aberrant Bryozoan has been made the subject of special study by Mr. Davenport. It was first noticed by Leidy in 1851, and later (1870 and 1884) further observations on its anatomy and physiology were made by him. The anatomy and non-sexual reproduction are now more fully described, and the following important conclusions are reached : Urnatella is closely related to Pedicellina. The Endoprocta are more primitive than the Ectoprocta, as the latter pass through stages resembling the adult condition of the former. The Endoprocta bear only a superficial resemblance to *Phoronis*. The true relationships of the Bryozoa are with the lowest worms, particularly with the Rotifera. The Bryozoa and Rotifera, together with the Mollusca, came from one phylum, and "after the Rotifer stem had branched off, the common Mollusco-Bryozoan stem produced tentacles on the lateral ridges; that the two groups then soon separated, the mollusca to undergo an extensive and complicated development, the Bryozoa to remain at a low level."

С. Е. В.

3. Lehrbuch der geologischen Formations-Kunde, für Studirende und zum Selbstunterricht, von Dr. EMANUEL KAYSER, Prof. Univ. Marburg. 386 pp. 8vo, with many figures of sections and fossils. Stuttgart, 1891. (Ferdinand Enke.)—A concise yet detailed account of the successive geological formations and their characteristic fossils.

4. Mineral Resources of the United States-Calendar year 1891. DAVID T. DAY. 630 pp. Washington: 1893 .- This is the ninth volume of the valuable series upon the Mineral Resources of this country. Like its predecessors it contains a large amount of useful information, compiled so as to be readily accessible. The article upon aluminum is especially full, and we note as of particular interest the statements made in regard to the occurrence of bauxite in this country, in Alabama, Georgia and Arkansas. As quoted from Prof. E. A. Smith, bauxite has been mined in Alabama since November, 1891, and in the year following some 3600 tons were shipped from Piedmont, while from Hermitage, Georgia, about 1300 tons had been mined up to July, 1892. The Alabama ore is stated to carry from fifty to sixty per cent of alumina. It occurs associated with limonite and kaolins in irregular beds, beneath the Knox dolomite of the Lower Silurian. The best known occurrences are near Rock Run Furnace in Cherokee County, and it has also been discovered near Jacksonville in Calhoun County. J. W. Spencer, State Geologist, states that the Georgia bauxite occurs in the residual clay from the decomposition of the Knox dolomite in the belt commencing near Adairsville and extending to the southwest. It occurs in pockets often of great extent and is frequently associated with kaolin, and at one locality with gibbsite. It is mainly in concretionary nodules forming large masses or small kidney-shaped lumps scattered through the clay. The Arkansas bauxite occurs, as stated by Prof. Branner, in the Tertiary in the neighborhood of eruptive syenite; it is pisolitic in structure, and varies somewhat widely in color and composition. A series of analyses from the different localities is also given (pp. 152–154).

5. Minéralogie de la France et ses Colonies, A. LACROIX. Tome premier (1re partie). 304 pp. 8vo. Paris, 1893. (Baudry et Cie.).—This is a work of much value, giving not only the results of earlier observations, but also the many original observations, especially on the physical side, of the indefatigable author. Minute detail in regard to special mineral localities is much needed, but can be given only in a work like this, which is devoted to a limited field.

6. Sodalite-syenite from Montana.—In the paper upon this subject by LINDGREN and MELVILLE, in the April number, the table giving the composition of albite and orthoclase near the top of p. 296 is stated incorrectly. It was intended to read as follows:

	Albite.	Orthoclase.
SiO <sub>2</sub>	68	66
Al <sub>2</sub> Ó <sub>3</sub>		19
K <sub>2</sub> O		13
Na <sub>2</sub> O	11	2

7. A Summary of Progress in Mineralogy and Petrography in 1892.—Professor W. S. BAYLEY's excellent notes, published in the monthly numbers of the American Naturalist, have been collected in pamphlet form, as in former years, and thus give a very convenient summary of the work done in the sciences named through the year. A topical index is added at the end.

8. A large Australian Meteorite.—It is stated that an enormous meteorite, weighing nearly one ton, from western Australia, has been received by Mr. J. R. Gregory, of Charlotte St., Fitzroy square. It is 4 feet 2 inches long by 2 feet 3 inches wide, and 2 feet 6 inches thick.—Knowledge, May 1st, 1893.

#### III. BOTANY.

1. Plants of Orizaba.—We have to note the issue of a posthumous work by the late Mr. Seaton, assistant Curator of the Gray Herberium of Harvard University. It comprises descriptions of his collections made during a journey to Mexico by the author. It is published in the Proceedings of the American Academy, Boston. G. L. G.

2. Die natürlichen Pflanzenfamilien.—The eighty-fourth installment of this work, to which we have made frequent reference, is the last one at hand. The publisher, Wilhelm Engelmann, of Leipsic, has spared no pains to maintain from the first, a very high standard of typography and illustration. It will be remembered that its earliest editor, EICHLER, died not long after the work was well in hand. It is now our sad duty to announce that the editoral staff has sustained another loss in the premature death of Professor PRANTL, who passed away on the 24th of February. Professor ENGLER will now have entire charge of the undertaking. Although this additional care must be a heavy burden on Professor ENGLER, it ensures for the volumes even greater unity of design and accomplishment than is possible under a double editorship. G. L. G.

3. Rainfall and Leaf-form.—Professor Stahl of Jena has published some interesting studies which he carried on at the mountain station of the Botanic Garden at Buitenzorg, Java. The mountain station is at Tjibodas, about 4,500 feet above sea-level, on a part of the volcanic Gedeh. No one who has seen the suddenness with which the rain which falls in the tropics is disposed of by the luxuriant foliage of a hillside can fail to be interested in Stahl's investigation. Some of the adaptations are among the most interesting in the whole range of vegetable forms, especially those which were connected with the rapid drying of the leaf itself in a comparatively moist atmosphere.

Professor Stahl has also busied himself with an examination of some of the means by which tropical plants protect themselves against the very heavy blows from rain-drops in the tropics. A good review of the paper, which appears in the Annals of the Buitenzorg Garden, is given in the 10th number (May 16) of Botanische Zeitung. G. L. G.

4. Turgescence and transpiration in fleshy plants; by ÉPHREM AUBERT, (Ann. Sc. Nat., vii Ser., T. 16).—The researches of this experimenter have brought out in a very clear manner certain relations which exist between the occurrence of vegetable acids in some fleshy plants and their slow transpiration. The fact that fleshy plants possess, especially in the dark, a notable amount of some organic acid, has been long known. To this acid, as it occurs in *Crassulaceæ*, Mayer gave the name of *isomalic*. In this Natural Order, it is associated with *tartaric* acid and tannin. In *Ficoideæ*, the acid is oxalic, while in Cactaceæ there is oxalic acid together with gums which later differ in their behavior to water, some being soluble, and others merely swelling in water.

The author concludes that the curve of water transpired by different parts of a fleshy plant has its minimum corresponding to the maximum content of organic acids and gums. Of course this resolves itself into the physical relations which depend on the effect of dissolved substances to retard evaporation.

G. L. G.

5. On the origin of Endogens from Exogens.—Rev. GEORGE HENSLOW, whose interesting work on the Origin of Floral Structures is well known to our readers, has a suggestive paper in the May (15th), number of the Journ. of the Linneau Society, on the vexed question of the relation in point of time between dicotyledonous and monocotyledonous orders. The subject is discussed from histological and morphological points of view and the following conclusions are reached. That endogens and exogens have had some common origin is, in the first place, obvious from the numerous points of agreement between their organs and tissues generally, as shown, e. g., in the structure of their flowers and anatomy of their roots, etc.; but the object of the present paper was to prove if possible, that there was a more special connection between endogens and an aquatic habit.

The coincidences in points of structure between endogens generally and the aquatic, and subaquatic exogens, as well as such exogens as may reasonably be supposed to have had an aquatic ancestry, are perhaps more numerous than the points of agreement with exogens generally. Nature supplies us with several "experimental verifications" in the alterations of structure in amphibious plants according as they live in water or on the land. These coincidences may be thought sufficient to prove that endogens have in the first place descended from very early types of exogens which preceded them; and that, secondly, the more immediate cause of their origin was an aquatic habit of life assumed by certain primitive exogenous plants.

To state the process of adaptation in as few words as possible, one might say that it was effected by means of the joint action of the external influences or forces of the environment and the internal responsive power of living protoplasm, so that when a terrestrial and aërial plant is grown in water, or a water-plant is transferred to land, the direct action of the new environment compels the plant (provided it can survive the change), to alter its structure so that the plant becomes at once adapted to the new medium. The change from land to water brings on therefore what may be called adaptive degenerations in every part of the plant. Conversely, a transference from water to land induces a tendency to restore the lost features, resulting, it may be, in a greatly enhanced and vigorous growth.

Whether there were several or few aquatic ancestors, or only one, the author does not venture to suggest, although he hints at the likelihood of there having been many. The difficulty in dealing with this question lies in the fact that at present it is impossible to trace affinities between the flowers of existing endogens and those of any existing orders of exogens. The conclusions of this important paper have been given above substantially in the words of the author, only a few unimportant changes having been made.  $\frac{1}{2}$  G. L. G.

#### IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The American Association for the Advancement of Science.—The next meeting of the American Association for the Advancement of Science will be held at Madison, Wisconsin, from August 16th to 23rd. The President is Professor William Harkness. This meeting is to be preceded by the meeting of the Geological Society of America, which is to be held at Madison on the 15th and 16th. It is to be followed by the World's Geological Congress to be held at Chicago during the fourth week of August, beginning on the 24th. Prof. T. C. Chamberlin of the University of Chicago is Chairman of the Committee.

2. Australasian Association for the Advancement of Science. —The next meeting of the Australasian Association for the Advancement of Science will be held in Adelaide, South Australia, commencing on September 25th, 1893. It will be presided over by RALPH TATE, F.L.S., F.G.S., Professor of Natural Science at the University of Adelaide. The following remarks are quoted from the circular issued, which gives the details in regard to the meeting :—

At the time fixed for the meeting, South Australia will be at its best. There is no better time at which to visit Australia than when spring is merging into summer. To naturalists, this time of year is specially attractive, and these are reminded that at the meeting of the Association they will come into contact with men of like tastes from all parts of Australia. Should visitors wish to prolong their trip, they are advised to visit during the months of October and November the principal objects of interest in the mainland, and in December, January, and February to pass on to New Zealand and Tasmania.

The general Hon. Secretaries who will give all needed information are: Professor A. Liversidge, of Sydney, and Professors E. H. Rennie and W. H. Bragg, of Adelaide.

3. British Association.—The next meeting of the British Association will be held at Nottingham, beginning September 13th. The President is Dr. J. S. Burdon-Sanderson.

4. Owen Memorial.—At a meeting of the Royal Society held January 21st, 1893, it was resolved, that "it is desirable that the eminent services of the late Sir Richard Owen in the advancement of the knowledge of the sciences of Anatomy, Zoology and Paleontology should be commemorated by some suitable memorial." This memorial is to consist primarily of a marble statue to be placed in the hall of the Natural History Museum in London. The Trustees of the British Museum have expressed their willingness to receive the statue, and donations to this end are now called for; they may be sent to the treasurer, Sir William H. Flower, Natural History Museum, London, S. W. It is stated that the sum already contributed amounts to nearly six hundred pounds.

5. Die Fortentwicklung der elektrischen Eisenbahn-Einrichtungen, von L. KOHLFÜRST. 296 pp. 12mo. Vienna, Pest, Leipzig, 1891. (A. Hartleben's Verlag).—This little volume belongs to the electro-technical library of A. Hartleben, which has been repeatedly noticed in these pages. It gives an account of the present state of the application of electricity to the railroad, including the use of signals of many kinds, of the telephone, and many allied subjects. 6. Gravity Research: Determinations of Gravity with halfsecond Pendulums on the Pacific Coast, in Alaska and at Washington, D. C., and Hoboken, N. J.; by T. C. MENDENHALL. 57 pp. Washington, 1892, (U. S. Coast and Geodetic Survey), Appendix no. 15. Report for 1891.—Professor Mendenhall discusses here the new half-second pendulum and describes the use at several stations, showing the high degree of accuracy obtainable with it. It is also shown that the free pendulum has a very important use as a time standard.

7. The Colors of Cloudy Condensation, by Prof. CARL BARUS. pp. 488-521. Reprinted from the American Meteorological Journal, March, 1893.—This interesting article is a full discussion of a subject which the author presented briefly in the February number of this Journal (page 150.)

8. Outlines of Forestry; or the elementary principles underlying the Science of Forestry. Being a series of Primers of Forestry; by EDWIN J. HOUSTON. 254 pp., Philadelphia, 1893. (J. B. Lippincott Co.).—There is certainly a most urgent call for enlightenment throughout this country in regard to the preservation and wise use of our forests, and a little book like the one in hand, which presents the whole subject in so popular a form as to appeal to all readers, should not fail to accomplish much good.

9. Naples Zoölogical Station.—Attention is called to the announcement in the advertising sheet, by Prof. Agassiz, that applications will be received from candidates who desire to occupy the table at the Naples Zoölogieal station, placed at the disposal of the faculty of the Museum of Comparative Zoölogy at Cambridge from October, 1893.

10. Krantz's Catalogue of Rocks.—Dr. Krantz of Bonn has recently issued an extended catalogue containing: first a systematic list of rocks arranged by Dr. W. Bonhus and Dr. Pohlig with literature references; also lists of special collections arranged according to particular subjects, and finally a catalogue of thin sections of authentic specimens in large numbers.

11. A Manual of Machine Drawing and Design, by DAVID ALLAN LOW and ALFRED WILLIAM BEVIS. 367 pp. 1893, London and New York, (Longmans, Green & Co.).—Students in mechanical engineering will find this Manual of great assistance. The various parts of machines of many kinds are described here with great fullness of illustration and exactness of statement, from the simplest form to the triple-expansion engine. Whether the subject is screws, bolts and nuts or the most complex boilers, the treatment is throughout admirably thorough and practical.

12. The Hawks and Owls of the United States in their Relation to Agriculture. Prepared under the direction of Dr. C. Hart Merriam, Ornithologist, by A. K. FISHER, M.D. 210 pp. Washington, 1893, (Government Printing Office.)—A handsomely illustrated work giving descriptions of the various hawks and owls known in the United States. Particular attention is given to the examination of the stomachs of many of the birds as showing the part they play in destroying insects, rodents, etc.

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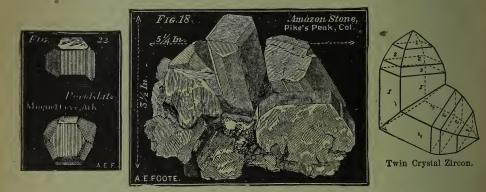
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but few countries where I have no customers. Many of the scientific men of the country recognizing the advantage of having such an exchange, have placed copies of their papers in my hands for sale on commission. Our lists of scientific books are sent free on light paper, except the 200 page Medical Catalogue, same prices as the Mineral Catalogue. Heavy paper, see page of book abbreviations.

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# AMERICAN JOURNAL OF SCIENCE

#### [THIRD SERIES.]

ART. XI.—The Use of Cupric Nitrate in the Voltameter, and the Electro-Chemical Equivalent of Copper; by FRED-ERICK E. BEACH.

[Contributions from the Sloane Physical Laboratory of Yale College.]

A MONG the voltameters in common use the silver voltameter gives results of a very high degree of accuracy, but is not conveniently used except for comparatively small currents. On the other hand the copper voltameter from the cheapness of materials and facility of manipulation finds convenient employment in the laboratory. As ordinarily used with the sulphate of copper, it is subject to certain irregularities due to the attack of the copper by the solution under some conditions, and the oxidation of the metal in others. For these reasons as well as for the fact that excellent deposits of metal are obtained from the nitrate of copper, even with great current densities, it seemed probable that this salt could be successfully used in the voltameter. The object of this paper is to show that cupric nitrate has some marked advantages over the sulphate. For purposes of comparison the results and conclusions of different experimenters will be passed in review.

Gore<sup>\*</sup> expresses the opinion that two independent forces act in the solution, one chemical the other electro-chemical. The action of the former is assisted by a rise of temperature. The loss of the anode is greater than the gain of the cathode, but the chemical corrosion of the anode is less than that of a sepa-

\* Nature, March 16, 1882.

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rate piece of copper without a current. The purely chemical corrosion of the cathode is more than that of the anode. The addition of any considerable amount of sulphuric acid had the effect of diminishing the weight of copper deposited.

Hammerl\* as the result of a detailed investigation comes to the following conclusions:

I. No change in the quantity of the deposit was observed when a blank platinum surface was substituted for one which had been covered with a deposit of copper.

II. The change of concentration of the solution caused by the passage of the current and the polarization dependent on it cannot be satisfactorily prevented by agitation. In boiling to agitate the fluid the deposit oxidizes almost completely to CuO, and partially indeed between  $40^{\circ}$  and  $60^{\circ}$  C.

III. The highest allowable current strength is 7 amperes per square decimeter. The distance between the plates should not be less than  $1.5^{\text{cm}}$ .

Gray<sup>†</sup> finds that the highest current-density desirable is one ampere to 50 square centimeters  $\left(=0.02 \ \frac{\text{amp.}}{\text{cm}^2}\right)$ . He obtains

the ratio  $\frac{Cu}{2Ag} = 0.2940$  and for the electro-chemical equivalent

of copper  $0.0003287 \frac{\text{gm.}}{\text{amp. sec.}}$  when silver is taken as 0.001118. He remarks "This would indicate a value not differing much from 0.0003290." He does not find as did Gore, that loss by chemical action is less when the current is flowing than when it is not. Copper was dissolved in the sulphate at the rate of  $0.02 \frac{\text{mgm.}}{\text{cm}^2. \text{ hr.}}$  Addition of sulphuric acid seemed to retard the loss when the density of the solution was between 1.1 and 1.15.

Gray<sup>+</sup> using a density of the sulphate solution of 1.15 to 1.18 with one per cent free sulphuric acid found that the equivalent depended on temperature and current-density in a manner which is exhibited by the following table. The factor  $10^{-7}$  has been omitted.

Area of cathode in		Tem	perature.		
sq. cm. per ampere.	2° C.	12° C.	23° C.	28° C.	35° C.
50	3288	3287	3286	3286	3282
100	3288	3284	3283	3281	3274
150	3287	3281	3280	3278	3267
200	3285	3279	3277	3274	3259
250	3283	3278	3275	3268	3252
300	3282	3278	3272	3262	3245

\* Wien. Ber., (2), lxxxviii, pp. 273-294. ‡ Phil. Mag., xxv, p. 179, 1888. † Phil. Mag., xxii, p. 289, 1886.

Vanni\* found that a solution of copper sulphate of density 1.12 with one per cent of free sulphuric acid dissolved copper, while a solution neutralized with copper hydrate gave an excess. Combining a liter of the normal solution with a half gram of that containing one per cent of the acid neither a gain nor loss could be observed in the weight of a piece of copper immersed in it.

The mean of six experiments with such a solution showed Cu = 0.2938, whence Cu equivalent = 0.0003284 with a cur-2Ag

rent-density between 0.011 and 0.002.

Cintolesi<sup>+</sup> observed that the solution of a copper plate in copper sulphate depends on the time and the current strength. In vacuo the amount of copper dissolved is less than in air. Oxygen was believed to have an essential influence on the phenomenon.

Shaw<sup>±</sup> using copper sulphate, and a current-density above  $0.025 \frac{\text{amp.}}{\text{cm}^2}$  found as a mean of fifteen experiments that the

ratio of  $\frac{2Ag}{Cu}$  was 3.39983 or Cu equiv. = 0.00032886.

It thus appears that the behavior of copper sulphate had been thoroughly studied; but no quantitative determination had been made with the nitrate, as far as the writer knows, although it had been stated by Smee and others, that the nitrate would bear a much greater current density than the sulphate.

The apparatus used in the experiments presently to be considered, may be briefly described as follows: the cathode was made from a piece of electrolytic copper about 2<sup>mm</sup> thick, by bending it so as to form three sides of a rectangle. This was immersed in copper nitrate contained in a glass beaker. The anode was usually a thin sheet of platinum though copper was occasionally substituted for it. The former was much preferred on account of the ease with which the copper is removed by dipping in nitric acid. After rinsing with water the platinum electrode may be dried by heating to redness in a Bunsen flame. The current was measured by the silver voltameter when small, and a Thomson Balance in a few instances when the total current was large. The value of the equivalent of silver used in calculating the numbers hereafter given was 0.0011181, the mean of the value 0.0011183 found by Kohlrausch§ and 0.00111794 the one given by Rayleigh.

\*Wied. Annal., x, p. 214, 1891. <sup>‡</sup> Phil. Mag., xxiii, p. 138, 1887. Phil. Trans., p. 439, 1884.

+ Beiblätter, xvi, p. 80, 1892. § Wied. Annal., xxvii, p. 57, 1886.

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#### 84 F. E. Beach-Use of Cupric Nitrate in the Voltameter,

It was found early in the course of the work that when the nitrate solution was freshly prepared, it had a tendency to dissolve copper, and that this tendency which was due to the solvent action of the solution itself or the presence of a small quantity of free acid, decreased after the copper electrode had been kept in the solution a sufficient length of time, and that this latter effect seemed to be facilitated by the passage of the current. On the other hand another difficulty to be contended with was the oxidation of the copper deposited after the solution had been used too many times or the current was pushed too far, causing in many cases a darkening or even perceptible blackening of the metal. It was however discovered that the blackening due to oxidation could be prevented by the addition of a small amount of ammonium chloride.

Experiments were now made in which the current density was varied through a considerable range with results which are given in the following table :

		Cur	rent-Density amperes.	7
No.	Solution	L <b>.</b>	cm <sup>2</sup>	Cu. Eq. $\times 10^{7}$
1	Cu2NO <sub>3</sub> nearly neutral w	vithout NH Cl,	0.035	3291
2		"	0.065	3291
3	"	"	0.144	3293
4	66	66	0.024	3293
5	66 0	"	0.83	3305
6	Cu2NO, with NH <sub>4</sub> Cl,		0.114	3290
7	° 66		0.074	3297
8	66		0.076	3298
9	66		0.094	3299
10	"		0.019	3290
11	61		0.048	3297

These values show no dependence on the current-density except No. 5 where the large value of the equivalent is best accounted for by oxidation caused by the excessive current. This deposit was badly fringed at the edge and easily detached. Numbers 1-5, made by repeated use of the same solution, show more uniformity than was at any other time obtained from a solution without ammonium chloride present. Attention may be called to what appears to be evidence of the neutralization of the solvent effect of the nitrate on the copper in the gradual but not always regular increase in the values obtained from the same solution in successive experiments.

Having now obtained a fair control of both the tendency to oxidation and solution, experiments were next undertaken with a view to determining the value of the electro-chemical equivalent. With the exception of Nos. 1–5 already quoted, the solutions used in obtaining the numbers given in the 1st Series were alike in that they were neutral with respect to the copper and contained  $NH_4Cl$ .

	First Series.		Second Series.
No.	Equivalent $\times$ 10 <sup>7</sup>	No.	Equivalent $\times 10^7$
1	3291	33	3294
2	3291	$^{34}$	3296
3	3293	35	3290
4	3293	36	3293
5	[3305]	37	3295
12	3296	38	3294
13	3297	39	3296
14	[3305]	40	3298
15	3293	41	3293
16	3294	42	3291
17	3296	43	3292
18	3294	44	3302
19	3292	- 45	3296
20	3300	46	3293
21	3299	47	3294
22	3299	48	3291
23	3291	49	329 <b>2</b>
24	3295	50	3293
25	3294	51	3292
26	3292	52	3293
27	3300	53	3292
28	3292	54	3291
29	3296	55	3298
30	3301		
31	3291		
32	3295		

The mean of the First Series, including Nos. 5 and 14, is  $3295.6 \pm 0.54$ . If these experiments be excluded we get  $3294.8 \pm 0.43$ .

Neutralization of the solution in the experiments described had been effected by repeated use. A readier method which suggested itself was to boil the nitrate in order to expel the air, allowing a piece of clean copper to stand in the hot solution until its solvent action had been exhausted. Such solutions were prepared and after the addition of a small amount of NH<sub>4</sub>Cl yielded values tabulated in the Second Series, the mean of which is  $3293.9 \pm 0.4$ .

In some cases the solutions employed were used many times so that the tests to which the nitrate has been subjected are in this respect particularly severe. There is good reason for supposing that the numbers would have been more consistent if a fresh solution had been used each time.

#### 86 F. E. Beach—Use of Cupric Nitrate in the Voltameter,

It is natural to inquire how the values found agree with the equivalent calculated from the atomic weight of copper.

The last named quantity has been investigated with great care by T. W. Richards\* with the following result:

If silver be taken as 108.00, oxygen as 16.000 and bromine 80.007

From	Cu:2Ag	he finds	Cu = 63.640
	Cu: (2AgBr)		Cu = 63.648
	CuBr <sub>2</sub> : 2Ag		Cu = 63.643
			Cu = 63.644

whence we get

 $\frac{\mathrm{Cu}}{\mathrm{2Ag}} = 0.29465$ 

and Cu Equivalent = 0.00032944when silver is taken = 0.0011181

Hence the value here found is substantially in accord with Richards'. In making this comparison it must be borne in mind that the present investigation was not undertaken for the purpose of finding the equivalent of copper but to determine how well the nitrate would serve as the electrolyte in the copper voltameter and that too, throughout a considerable range of conditions. That these conditions when working with such a sensitive metal as copper were sometimes unfavorable to uniformity of result may be sufficient to explain the amount of variation from the mean. The probable error of a single observation in the Second Series is  $\pm 1.9$ .

Further experiments were tried to determine the effect of variations in the temperature. Here again it is to be remembered that the solutions were not freshly prepared. A considerable change of temperature either up or down seemed to favor oxidation, but more particularly the latter, probably on account of the increase in concentration of the salt when cooled. Still even this was in great measure prevented by a sufficient addition of the ammonium chloride.

No.	Solution.	Temperature.	Equivalent $\times 10^{7}$ .
56	Cu2NO, with NH <sub>4</sub> Cl	19°	3296
57	Same	6	3297
<b>5</b> 8	Same	34	3292
59	Same	29	3321
60	Another solution	18	3291
61	Same	36	3297
62	Same	37	3296
63	Same	6	3313
64	Same	10	3307
65	A different solution	40	3291
66	Same	to	3292

\* Proc. Amer. Acad., xxiii, p. 177. Ibid, xxv, p. 212.

From these experiments we may conclude that a moderate change of temperature is not a critical matter.

The First and Second Series were made at the temperature of the room which did not vary much from 19° C.

The following method is recommended for the preparation of the solution : Dissolve copper nitrate, the purest obtainable, in distilled water. Boil for a short time to expel the air and keep at a temperature of 100° C. for an hour or two in the presence of bright metallic copper in order to completely neutralize the solution. When ready for use it should have a density of about 1.53. Add a saturated solution of  $NH_4Cl$  at about the rate of 1 drop to  $100^{\circ\circ}$  of the nitrate. Just the proper amount of ammonium chloride it is not easy to specify. If too much be present the deposit will discolor on drying; if too little, bubbles will collect on the cathode or the deposit will oxidize in the solution. Perhaps the surest way is to try a preliminary experiment, adding the  $NH_4Cl$  till the plate begins to show discoloration on drying.

If the solution is to stand the anode may be left in it. Care should be taken to exclude the air.

On removal from the solution the cathode should be washed thoroughly in running water and drained until it may no longer be said to be wet, after which gentle heat should be cautiously applied until all moisture is removed.

The advantages possessed by the nitrate may be enumerated as follows:

1st. The weight of copper deposited does not appear to depend on the current density.

2d. It permits the use of a high current-density.

The limit is not easily stated. When 0.25 amperes per square centimeter is reached the cathode needs watching, for it will fringe at the edge but does not become powdery.

No way was found to prevent the branching with a high current-density.

A greater amount of  $NH_4Cl$  should be present when the current density is increased.

3d. The weight of copper is practically independent of the temperature between  $10^{\circ}$  and  $35^{\circ}$  C.

The tendency to oxidation is increased by lowering the temperature but this may be easily counteracted by the addition of more NH<sub>4</sub>Cl.

4th. The solution may be used a number of times.

5th. The equivalent agrees to four figures with that calculated from the best chemical determinations, viz :

 Richards
 Eq. =  $(3294 \cdot 4 \pm 0 \cdot 1) \times 10^{-7}$  

 First Series
 Eq. =  $(3294 \cdot 8 \pm 0 \cdot 43) \times 10^{-7}$  

 Second Series
 Eq. =  $(3293 \cdot 9 \pm 0 \cdot 39) \times 10^{-7}$ 

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1

The purity of the nitrate as a condition of success is to be emphasized. One specimen tried, which contained nitrite, was absolutely worthless with the foregoing treatment.

To see what CuSO, would do under circumstances similar to those in which the nitrate was studied, a saturated solution of the sulphate was rendered neutral by the copper hydrate precipitated on addition of ammonia.  $\rm NH_4Cl$  was added until the deposit was as bright and lustrous as that formed in an acid sulphate solution.

Three such experiments yielded

Eq.	=	$3295 \times 10^{-7}$
Eq.	=	$3293 \times 10^{-7}$
Eq.	=	$3294 \times 10^{-7}$

Two other experiments in circuit with the nitrate showed

		Sulphate.	Nitrate.
		gms.	gms.
Copper	deposited	0.4722	0.4719
do.	do.	0.261	0.5667

These values tend to confirm the result obtained from the nitrate; at least they do not contradict it.

In conclusion I wish to express my thanks to Professor A. W. Wright, under whose direction the preceding investigation was made, for his many kind and helpful suggestions.

Sloane Physical Laboratory, June 1st, 1893.

ART. XII.—On the Double Halides of Arsenic with Casium and Rubidium; and on some Compounds of Arsenious Oxide with the Halides of Casium, Rubidium and Potassium; by H. L. WHEELER.

No compounds of arsenious halides, with alkaline halides, have been definitely described. Nicklès\* in his work on the bromides and iodides of arsenic, antimony and bismuth, states that these salts combine with alkaline bromides and iodides respectively, but in the case of arsenic he gives no analyses of the compounds which he obtained and he does not describe the methods that he used in preparing them. He does not even state with what alkaline halides he performed his experiments. Emmet<sup>+</sup>, Harms<sup>+</sup>, Schiff and Sestini<sup>§</sup> have described

† This Journal, I, xviii, 58.

‡ Ann. Chem. Pharm., xci, 371.

§ Ibid., 228, 72.

<sup>\*</sup> Compt. Rend., xlviii, 839; Journ. Pharm., III, xli, 142; Rép. chim. pure, i, 366.

compounds of arsenious oxide with potassium halides, but this class of bodies has been most thoroughly studied by Rüdorff.\* His results indicate the existence of two types of this class of compounds, the first containing one molecule of alkaline halide to one of arsenious oxide, the other having these constituents in the ratio 1:2. In the present investigation a complete series of the cæsium and rubidium oxyhalides of the 1:1 type was obtained, while the formation of the 1:2 type was not observed. There is evidently a gradation in stability from the oxychlorides to the oxyiodides, the stability increasing with increasing atomic weight of the halogens. Attempts to prepare double halides of pentavalent arsenic were without success.

The new compounds to be described in this article are the following :

$3$ CsCl . $2$ AsCl $_{3}$	3CsBr.2AsBr <sub>3</sub>	3CsI. 2AsI
$3$ RbCl . $2$ AsCl $_{3}$	3RbBr.2AsBr <sub>3</sub>	3RbI. 2AsI <sub>3</sub>
$\begin{array}{c} \mathrm{CsCl}.\mathrm{As_2O_3}\\ \mathrm{RbCl}.\mathrm{As_2O_3} \end{array}$	$\operatorname{CsBr}_{\operatorname{a}}\operatorname{As}_{2}\operatorname{O}_{3}$ $\operatorname{RbBr}_{\operatorname{a}}\operatorname{As}_{2}\operatorname{O}_{3}$	$\operatorname{CsI.As_2O_3}_{\operatorname{RbI.As_2O_3}}$

The compound  $As_2O_3$ . KI which had not been observed by Rüdorff<sup>+</sup> was obtained in attempts to prepare a double iodide of potassium and arsenic.

It is to be noticed that only one type of double halides was obtained. This type corresponds to the most readily prepared double chloride of cæsium with antimony, described by Remsen and Saunders<sup>+</sup>, and of cæsium and bismuth, described by Remsen and Brigham.§ Many attempts were made to prepare arsenic double halides of other types than this single one, but these have invariably been without success, although several types of antimony and bismuth double halides have been described.

It has been shown in several instances by Wells and Wheeler that cæsium and rubidium halides form more stable or more complete series of double salts than the halides of the other alkali-metals. This fact is again well illustrated in the double halides of arsenic, for the cæsium and rubidium double halides are prepared without difficulty, while with potassium no double halides were obtained.

Methods of preparation.—To prepare the double halides, a strong acid solution is necessary, in order to prevent the decomposition of the arsenious halide and the consequent formation of oxy-compounds. The double halides are less

<sup>\*</sup>Ber d. Deutsch. Chem. Ges. xix. 2668; ibid. xxi. 3053.

<sup>+</sup> Loc. cit. § Ibid., p. 164.

<sup>‡</sup> Am. Chem. Jour., xiv, 152. This Journal, 111, xhii. 475; IJI, xliv, 42.

soluble in the strong than in the dilute halogen acids. Excess of one or the other of the constituents has no effect on the composition of the products obtained. The formation of  $As_2O_3$  compounds was observed on treating the double halides or a solution of the constituents in strong acids, with water or dilute acids. The oxygen compounds are difficultly soluble in dilute acids, strong acids convert the cæsium and rubidium compounds into the double halides.

## Method of Analysis.

The salts were filtered on the pump and without delay were carefully freed from the mother liquor by pressing on paper. They were then dried in the air. In no case was water used to wash them. In order to determine arsenic the salt was dissolved in the cold in HCl sp. gr. 1.1 and hydrogen sulphide passed in for about one hour; then a little alcohol was added. the whole was warmed on the water bath for a short time, in order to drive off the excess of hydrogen sulphide and effect the separation of the last traces of arsenious sulphide. The sulphide of arsenic was collected on a Gooch filter and after washing with water, alcohol and carbon disulphide it was dried at 100° and weighed. Sulphuric acid was added to the filtrate and the alkali-metal determined as normal sulphate by evaporating and igniting the residue in a stream of air containing ammonia. The halogens were determined in a separate portion as silver halides in the usual manner.

### The Double Halides.

Cæsium and Rubidium Arsenious Chlorides: 3CsCl. 2AsCl. and 3RbCl. 2AsCl<sub>3</sub>.—These have a pale yellow color like the corresponding antimony and bismuth double chlorides. The cæsium salt was obtained by dissolving 250 gms. of CsCl in dilute HCl. 2 grams of As<sub>2</sub>O<sub>3</sub>, in dilute HCl were then added. This produced a precipitate which dissolved on the addition of about 2 liters of hot HCl sp. gr. 1.1. On cooling, light yellow crystals were deposited. A portion of these was recrystallized from a strong HCl solution of AsCl. The rubidium salt was prepared in the same manner, except that much stronger solutions were required. Saturated solutions of rubidium and arsenic chlorides in 20 per cent HCl produce no precipitate on mixing but if concentrated HCl is added, brilliant spangles of the double salt separate. The analysis of these products gave :

	Prepared excess of		Prepared with excess AsCl <sub>3</sub>	Calculated for $3$ CsCl $.2$ AsCl <sub>3</sub>
Cs	46.14	45.27	45.09	45.94
As	17.15		17.11	17.27
Cl	36.89	36.74	36.12	36.79
As		20.14	Calculat 3RbCl2 35 20 44	AsCl₃ 33 66

Both salts can be recrystallized from hydrochloric acid of sp. gr. 1.1. 100 parts of HCl sp. gr. 1.2 dissolve .429 parts of the cæsium salt and 2.935 parts of the rubidium compound. Since the corresponding potassium salt apparently does not exist, these solubilities suggest a convenient method for obtaining cæsium and rubidium free from potassium.

Casium and Rubidium Arsenious Bromides: 3CsBr.  $2AsBr_{s}$  and  $3RbBr. 2AsBr_{s}$ .—These are amber-yellow, the shade being somewhat darker than that of the chlorides. They are most conveniently prepared by using an excess of the alkaline halide. Strong hot solutions of the alkaline bromides were made in about 40 per cent HBr. On adding crystals of  $AsBr_{s}$ these melted but soon solidified to a yellow mass of the double halide. This dissolved on boiling, and, on cooling, brilliant yellow crystals were obtained. These compounds can be recrystallized unaltered from strong HBr. Analysis gave :

			Calcula	ted for
		Found.	3CsBr.2	$AsBr_3$
	Cs	31.91	31.	44
	As	11.89	11.	82
	Br	56.94	56.	74
	Prepared wi excess of Rb		red with of AsBr <sub>3</sub>	Calculated for 3RbBr.2AsBr <sub>3</sub>
Rb	23.35			22.77
	12.55			13.31
Br	63.97	6	4•43	63.92

Casium and Rubidium Arsenious Iodides:  $3CsI.2AsI_s$ and  $3RbI.2AsI_s$ .—These are deep red, the larger crystals of the casium compound are more opaque and appear black. To prepare these compounds the normal alkaline iodides were dissolved in strong colorless hydriodic acid and these solutions were then saturated boiling with crystals of  $AsI_s$ . Unless the hydriodic acid is decolorized the product obtained in the case of the casium salt is generally impure, being mixed with  $CsI_s$ .\*

\* This Journal, xliii, 17; Zeitschr. f. Anorg. chem., i, 85.

A well crystallized product of the double cæsium salt was obtained by preparing the salt in the presence of considerable alcohol. Analysis of these compounds gave

		Calc. for 3CsI.2AsI <sub>3</sub>				Calc. for I.2AsI <sub>3</sub>
Cs	24.38	23.28	Rb	16.86		16.55
As	8.92	8.87	As	9.96	10.60	9.68
I	67.23	67.55	I	73.65		73.77

An attempt was made to prepare potassium arsenious chloride by mixing solutions of potassium chloride and arsenious acid, saturated solutions of these substances in concentrated HCl being used for the purpose. No precipitate was thus produced, and, on concentrating the solution, potassium chloride was deposited. Aqueous solutions of potassium chloride, when added to solutions of arsenic trioxide in concentrated HCl, gave precipitates consisting chiefly of As<sub>2</sub>O<sub>3</sub>. Analogous experiments with potassium bromide and arsenious bromide gave similar results, and operating in the same way with KI and AsI, in concentrated HI solutions, nothing but crystals of AsI<sub>3</sub> or mixed crops of AsI<sub>3</sub> and KI were obtained. Similar negative results, in respect to the formation of double halides of ammonium and arsenic, have been obtained by Wallace.

Compounds of Arsenic Trioxide with Alkaline Halides,  $CsCl. As_2O_3$  and  $RbCl. As_2O_3$ :—When a hot saturated aqueous solution of 25 grams of cæsium chloride was saturated with  $3CsCl. 2AsCl_3$ , a finely divided white precipitate was formed on cooling, (Analysis 1.) When 6.5 grams of the double chloride were dissolved in  $800^{\circ\circ}$  of a cold-saturated solution of  $As_3O_3$  in HCl of sp. gr. 1.1 by the aid of heat, a similar precipitate was obtained (analysis 2). Products intermediate in composition were obtained by recrystallizing the double halide from water (analysis 3), from 10 per cent HCl (analysis 4) and from 15 per cent HCl (analysis 5).

	1.		2.	3.
Cs 41.51	41.85 41.7		25.56	34.29
As 35.59	34.58 35.3	7	47.64	43.05
Cl 11·46	11.3	1	11.64	8.86
O[11·44]	[11.5	7]	[15.16]	[13.80]
			Calcu	lated for
	4.	5.	CsC	$1.As_2O_3$
Cs	35.30	33.92	3	6.29
As	39.14	38.10	4	0.93
Cl	10.63	11.42		9.68
0	[14.93]	[16.56]	1	3.10
1 701 11	1.0		0.01	

+ Phil. Mag. IV, xvi, 358; xvii, 122, 261.

The analyses show a considerable variation from the composition required by the formula, the products made under the extreme conditions giving ratios of arsenious oxide to cæsium chloride of 3:4 and 3:2 instead of 1:1. The conditions varied so widely however that it seems fair to assume the existence of a 1:1 compound.

When the double chloride of rubidium was recrystallized from about 15 per cent HCl, a white crystalline crust was obtained on slowly cooling. This gave analytical results agreeing with the formula RbCl.  $As_2O_3$ .

		RbCl. As <sub>2</sub> O <sub>3</sub>
Rb	26.90	26.80
As		47.03
Cl	11.41	11.13
0		15.04

Under the microscope these compounds appear as irregular grains or plates, of indefinite crystalline form.

CsBr.  $As_2O_s$  and RbBr.  $As_2O_s$ .—When the double bromides are recrystallized from water, or dilute HBr, they yield these oxy-compounds, and these generally separate in the form of a white crust on the bottom and sides of the beaker. Analysis of such products gave:

3CsBr . 2A recrystalliz from wat	sBr <sub>3</sub> recry zed from	Br.2ASBr <sub>3</sub> rstallized m CsBr lution.	Calculated for CsBr.As <sub>2</sub> O <sub>3</sub>
Cs 32.	42		32.36
As 36.	52		36.50
Br 19	57	19.59	19.46
0 [11-	49]		11.68
	tbBr.2AsBr₃ m dilute HBr.	3RbBr. 2AsBr <sub>3</sub> from water.	Calculated for RbBr.As <sub>2</sub> O <sub>3</sub>
Rb	24.24	16.56	23.52
As	40.06	50.74	41.27
Br	24.53.	15.91	22.01
0	[11.17]	[16.79]	13.20

It is to be noticed that the product obtained by recrystallizing 3RbBr. 2AsBr<sub>3</sub> from water is impure, while the cæsium compound made in the same way corresponds to the formula. This is an illustration of the greater tendency of the cæsium halide to form double salts than in the case of the rubidium halide. Both these compounds are white, but the rubidium compound turns somewhat yellow on drying. Under the microscope, six sided plates were seen in the case of the cæsium compound when the solution was slowly cooled. There were also observed hexagonal crystals with a short columnar rhombohedral habit. They were uniaxial with weak, negative double refraction. The rubidium compound was also obtained in hexagonal crystals showing rhombohedral symmetry and weak negative double refraction.

 $CsI. As_2O_3, RbI. As_2O_3 and KI. As_2O_2$ .—The formation of these compounds was observed when dilute hydriodic acid solutions of the alkaline iodides were mixed with dilute acid solutions of AsI<sub>3</sub>. If the solutions are mixed while hot these double salts separated on cooling in the form of crystalline yellow crusts on the bottom and sides of the beaker. These crystals are generally somewhat larger than those of the compounds of As<sub>2</sub>O<sub>3</sub> with the chlorides and bromides. Under the microscope they exhibited the form of six sided plates. These show a strong negative double refraction.

The potassium compound also appeared in the form of six sided plates; these remained dark when rotated between crossed nicols. They were too small to afford an axial figure as the largest plates did not exceed  $0.01^{\text{mm}}$  in diameter. They are probably hexagonal. Analysis gave:

	Calculated for CsI.As <sub>2</sub> O <sub>3</sub>
Cs	29.04
As	32.75
I 28.94	27.73
O [9·74]	10.48
	Calculated for RbI . As <sub>2</sub> O <sub>3</sub>
Rb 20.35	20.83
As	36.54
I 31.94	30.83
O [10·93]	11.70
	Calculated for $KI \cdot As_2O_3$
K 10.75	10.74
As 42.85	41.20
I 34·13	34.88
O [12·27]	13.18

#### Crystallography.

The crystallization of the cæsium and rubidium arsenious halides is hexagonal. They were all measured and found to be isomorphous. In general the habit was holohedral, although in the case of cæsium arsenious bromide it is rhombohedral. All these salts show a pronounced basal cleavage, and plates parallel to this, examined with the stauroscope, are uniaxial: the double chlorides and bromides show a weak negative double refraction while the double iodides are positive. The forms observed are as follows:

С	0001	0	$\gamma^*$	1011	1
α	$11\bar{2}0$	i-2	z	0111	-1
m	$10\bar{1}0$	Ι	p	$20\overline{2}1$	$^{2}$

The steep pyramid p was found only on the iodides. The following table gives the lengths of the vertical axes.

	$\alpha$ .	:	С
3CsCl. 2AsCl	1		1.209
3RbCl.2AsCl <sub>3</sub>	1		1.210
3CsBr. 2AsBr	1		1.219
3RbBr. 2AsBr	1		1.220
3CsI.2AsIs	1		1.244
3RbI.2AsI	1		1.243

A comparison of the above axial ratios shows the interesting fact that the substitution of rubidium for cæsium produces no appreciable effect in the lengths of the axes, and that in this series the vertical axes lengthen as the atomic weight of the

halogens increases. The crystals were sufficiently stable to yield good measurements, although on long exposure they usually lose their luster. In the lists of measurements the angles chosen as fundamental are noted by an asterisk.

3 CsCl. 2AsCl,.--This salt was made in crystals about 1-2<sup>mm</sup> in diameter. The forms observed are m, a, r, z and A careful search was made for in-С.

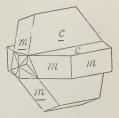
dications of a rhombohedral development of the faces r and  $z_i$ but none was found. Apparently they are always holohedral in their development, fig. 1.

		Measured.	Calculat
mrc	1010 ~ 0001	90°	90°
c ~r	0001 - 1011	*54 24'	
$r \star m$	1011 - 10-0	35 39	35 30
$m \land z$	1010 - 0111	66 3	66
TAZ	1011 - 0111	47 53	47 5

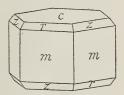
There is a rather poor prismatic cleavage and plates parallel to this show parallel extinction.

3RbCl.2AsCl<sub>s</sub>.—This salt was made in crystals up to about 5<sup>mm</sup> in diameter. The forms observed are c, m, r and z. The faces r and z were seldom present, but when these did occur it could not be seen whether they exhibited rhombohedral symmetry or not. Penetration twins are common, the twinning plane being the rhombohedron 0111, fig. 2.





2.

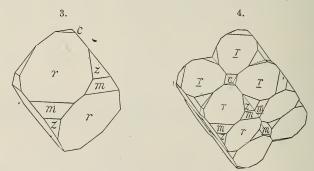


1.

		Measured.	Calculated.
c ~ c (twi	n) 0001 ~ 0001	*71° 3'	
c r	0001 - 1011	54 21	$54^{\circ} 28\frac{1}{2}'$
$m \wedge r$	$10\overline{1}0 \land 10\overline{1}1$	35 39	$35 31\frac{1}{2}$

On examining this salt in convergent polarized light a uniaxial cross is seen whose arms are not black but a deep and brilliant blue, the character being negative. When examined in monochromatic red light the crystals are nearly isotropic, the double refraction being extremely weak and probably negative. In blue light, however, a distinct cross is seen accompanied by axial rings. This difference between red and blue explains the colored cross seen in white light. Sections parallel to the  $\dot{c}$  axis show the deep peculiar blue characteristic of uniaxial bodies with the above mentioned optical properties.

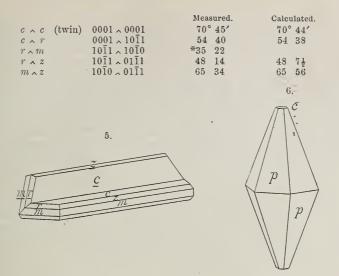
 $3CsBr.2AsBr_{s}$ .—This salt was made in crystals up to  $1\frac{1}{2}$ <sup>mm</sup> in diameter. The forms observed are c, m, r and z This is the only salt of the series that has a rhombohedral habit and as the angle of the rhombohedron is nearly 90° the crystals look like cubes. Fig. 3 shows an ideal combination of r with m, z and c. This form was not observed as the crystals are



invariably twins. An ideal representation of the twinning is given in fig. 4. The r faces were so curved and striated that no exact measurements could be made from them.

		Measured.	Calculated.
$m \land z$	0110 ~ 0111	*35° 23'	
2 ~ 2	1011 ~ 1101		89° 50′

 $3RbBr \cdot 2AsBr_{s}$ .—This salt was made in small crystals, up to  $2^{mm}$  in diameter. The forms observed were c, m and r. The crystals were made in two habits. When prepared with an excess of RbBr it separates in prismatic crystals which resemble the form of cæsium arsenious chloride, fig. 1. In one experiment by using an excess of AsBr<sub>s</sub> contact twins were obtained. Here the twinning plane is the unit rhombohedron as in fig. 2, but some of the faces are lengthened parallel to the edge between the two basal planes (fig. 5).



 $3CsI.2AsI_s$ .—This salt was made in beautiful crystals up to  $3^{mm}$  in length. The forms observed are p and c. The habit is that of a steep doubly terminated hexagonal pyramid, with the basal planes small or wanting. Often the middle edges are rounded by oscillatory combinations of the pyramids giving rise to horizontal striations. There was no indication of a prism or of a rhombohedral development of the pyramidal faces.

		Measured.	Calculated.
$c \land p$	$0001 \ 100\overline{2}1$	*70° 49'	
$p \wedge p$	$20\bar{2}1 \land 20\bar{2}\bar{1}$	38 19	38° 22′
pAp	$20\overline{2}1 \land 02\overline{2}1$	$56 24\frac{1}{2}$	$56\ 21\ 34''$

This salt is without optical anomalies and no pleochroism was observed.

 $3RbI. 2AsI_{s}$ .—This salt was prepared in very small crystals, not over  $1^{mm}$  in length. The forms observed were c, m and p. The habit is similar to fig. 6 but usually the middle edges are replaced by the faces of the prism m or are rounded by horizontal striations.

		Measured.	Calculated.
$p \land p$	$20\bar{2}1 \land 02\bar{2}1$	*56° 21'	
c ~ p	$0001 \land 20\bar{2}1$	70 47	70°
$p \wedge \overline{m}$	2021 ~ 1010	19 12	20 56'

Optically, this salt shows anomalies. Basal cleavage plates between crossed nicols are not dark but light and remain so during revolution. In convergent light the locus of an optic axis is seen in the center of the field coinciding with the ver-

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, NO. 272.-AUGUST, 1893.

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tical axis c. The bisectrix lying nearest this axis is that of least elasticity C. The salt is not, however, properly biaxial, the plane of the optic axes is sometimes parallel, sometimes perpendicular to the edge of the prism. Moreover this direction often changes from place to place in the same plate and at times no bar is seen, but a black dot in the center of the field surrounded by rings. Such behavior can be explained by supposing the crystal to be in a condition of internal strain. Sections parallel to the prism sometimes remain light between crossed nicols, sometimes extinguish at varying angles and show a slight pleochroism, the absorption being  $\varepsilon > \omega$ ; the color a deep reddish orange.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the present investigation and to Prof. S. L. Penfield under whose direction the crystallography of these salts was investigated. The author is also indebted to Mr. L. V. Pirsson for aid in the optical description of these salts.

Sheffield Scientific School, March, 1893.

ART. XIII.—On Mackintoshite, a new thorium and uranium mineral; by WM. EARL HIDDEN: with analyses by W. F. HILLEBRAND.

*History.*—It is three years since an alteration product<sup>\*</sup> of the new species here described was announced jointly, by the late James B. Mackintosh,<sup>†</sup> and the writer, under the name of "thoro-gummite." In the interim a most diligent search has been made at the locality in Llano County, Texas, to discover the mineral in quantity, and also, if possible, the parent mineral from which it was derived. In an endeavor to find some fragments of the unaltered mineral, I broke up nearly a kilogram of the thorogummite, with the result of finding less than one gram of a black mineral which, from the position it occupied within the thoro-gummite, we concluded must represent the original species. I note here that some irregular cores, of a dark brown translucent mineral, were also found but they proved to be very soluble and not essentially different from the enclosing thoro-gummite. They had a density of 4.50.

Some chemical tests, then made by the writer, proved the black mineral to be practically unaffected by hydrochloric or sulphuric acids and the density as then determined was 5.361.

\* This Jour., vol. xxxviii, Dec., 1889, p. 480.

+ He died on April 15, 1891; see this Journal, xli, 444.

Upon fusing a portion with sodium bisulphate a solution was obtained and it was thus found to be a silicate containing about 23 per cent of uranium oxide (calculated as  $UO_2$ ), about 46 per cent of thoria and a small per cent of the "rare earths."

No further data were then obtained from the scant material in hand but its relation to thoro-gummite was made evident. It was among fresh shipments of the various thoria and yttria minerals, made direct from the locality (Llano County, Texas) that this mineral was again found and further analytical work made possible. The new material was unexpectedly found deeply embedded in massive cyrtolite and associated with fergusonite. None was found embedded in the new crystals and masses of thoro-gummite. Some fifty kilograms of the broken cyrtolite were thoroughly searched through with the result of finding only about two grams of pure material and this came mainly from one mass, which had a very thin coating of thorogummite. A few selected fragments had a specific gravity of 5.438, [one portion weighed 0.35 gram.] As the mineral was so scarce it was set aside to await an opportunity when it could be given careful investigation. Later, by using small quantities, the physical characters were made out as follows.

Description.—The mineral is opaque and black, but not quite so dull in luster as the associated black cyrtolite which it resembles to a very remarkable degree. A strong lens is necessary to distinguish the two. Its hardness is about 5.5. No trace of cleavage has been observed. Its fracture is minute sub-conchoidal to hackly. Density = 5.438 at  $21^{\circ}$  C. (for the material analyzed by Hillebrand, see beyond.) Its form, as is often evidenced by the thoro-gummite, is tetragonal and closely resembles zircon and thorite in habit and angle. Square prisms, sometimes 1<sup>cm</sup> thick, with a simple pyramid are all the forms thus far observed. It also occurs massive, nodular and filling veins in cyrtolite and fergusonite embedded in a coarse pegmatite. Under the blowpipe, it is infusible but becomes fissured in all directions without intumescence or decrepitation.

In powder the mineral is not entirely decomposed by any one acid. Sulphuric acid attacks it quite strongly but the gelatinous silica set free protects it from further action. Hillebrand has observed however that if nitric acid is added, speedy and complete solution results.

Chemical Composition.—For the chemical investigation of this mineral I am indebted to Mr. W. F. Hillebrand, whose important contributions to the chemistry of uranium minerals are well known. I quote his report and analyses in full.

"Of the dull black mineral supposed by Mr. Hidden to be the parent of thoro-gummite but nine-tenths of a gram was available for analysis after careful hand-picking under the lens. It was almost entirely free from recognizable impurity and had a density of 5.43 at  $21.4^{\circ}$  C.

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

Considering that the limited sample had to be divided into three portions in order to estimate the constituents tabulated below, it is not perhaps surprising that the analysis should present a loss of three and one-half per cent. The presence of even the little phosphoric acid shown renders the analytical operations by which the silica and bases are determined extremely complicated, particularly when zirconia and yttria are present. Precipitates are then obtained which under similar conditions the other earth bases do not give, and thus separations and identifications are rendered more difficult and losses are almost inevitable. It is therefore not at all certain that the very considerable loss is to be sought in some constituent not enumerated; it is more probable that it should be distributed somewhat unevenly over a number of those given, silica and lead oxide excepted, they being without doubt nearly correct. The following observations, however, may be of importance in this connection. After sealing the tube in which was the sample serving for the estimation of the oxidizable constituents a slow but long continued evolution of gas was observed, just as in the case of most uraninites when similarly treated, but owing to the very small quantity of powder in the tube-only 15 gram-it could not be proven that the gas was nitrogen and not CO<sub>2</sub>. The latter it should not be, for thorogummite, the direct alteration product of the mineral, is free from it according to Hidden and Mackintosh's analysis. In any event its amount is probably very small.

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

a	u b	Thoro-gummite (H. & M.)
SiO <sub>2</sub> 13.9	0 13.92	SiO <sub>2</sub> 13.085
UO <sub>2</sub> 22.4	40 21.86†	UO <sub>3</sub> 22.43
ZrO <sub>2</sub> ?	8 ] '	ThO <sub>2</sub> 41.44
$\left\{\begin{array}{c} \text{ThO}_2\\ \text{CerO}_2\end{array}\right\}$	0*	Al <sub>2</sub> O <sub>3</sub>
00203 + 1	lost	Fe <sub>2</sub> O <sub>3</sub>
$\begin{array}{c} \text{La}_2\text{O}_3\\ \text{Y}_2\text{O}_3\end{array}$ groups 1.8	an l	$(Ce, Y)_2O_3$ etc. 6.69 (At. W. 135)
$Y_2O_3$ $\int groups \dots rc$	,° J	PbO 2·16
Pb0		CaO
FeO 1.1	5 ‡	$P_2O_5$
CaO	9 44	$H_2O_{$
MgO ·1	0 13	Moisture 1.23
K <sub>2</sub> O		
$(Na, Li)_2O$	is )	98.325
P <sub>2</sub> O <sub>5</sub>	37 ·46	
$H_2O$ above 100° C. 4.3	-	
$H_2O$ below 100° C. ·5	0 .35	
96.2	0	

Taken by themselves these results are incapable of translation through the medium of molecular weights into any precise formula, but they become of interest when compared with the accompanying analysis of thoro-gummite by Hidden and Mackintosh.§ It is then seen that the opinion of Mr. Hidden regarding the derivation of thoro-gummite from the present mineral was fully justified. It is in fact remarkable, considering the great molecular alteration that must have taken place, as determined by the totally different appearance of the two minerals, that so little loss of substance has taken place. Almost the sole change has consisted in an oxidation of uranous oxide and an increase in the hydration. These facts render not altogether safe the assumption above made that all uranium and iron in the new mineral exist there in the lower forms of oxidation, and they furthermore indicate that the black mineral itself may have already undergone oxidation and hydration without this being manifest to the eye-a supposition which is strengthened by the loss at 100° C. of half a per cent of water, and in fact by the intimate union which existed between the two minerals when received. Such material alteration without corresponding physical evidence of it. seems to be common among uraninites. The original condition of the mineral may then have been one in which uranium and iron were entirely in the lower state of oxidation and in which

<sup>\*</sup> The precipitate by potassium hydroxide was pure white after long action of chlorine. It nay, however, have contained a trace of cerium.

 $<sup>\</sup>dagger$  Would be slightly increased by uranium which was not separated from the earths.

 $<sup>\</sup>ddagger$  The estimation of iron miscarried, but the amount was unquestionably less than in a.

<sup>§</sup> This Journal, xxxviii, 480, 1889.

water was possibly absent. It is to be hoped that opportunity may yet be afforded for a more thorough examination of this mineral, which though apparently allied to thorite and uranothorite, is distinguished from them chiefly by greater content in uranium and by a higher degree of basicity."

Discussion of Composition.—It may be of interest to add a few words as to the relation of this mineral to thoro-gummite, although in view of the loss of 3.5 per cent in the analysis there is an unavoidable element of doubt attached to any formulæ which may be deduced. However, if the larger proportion of the loss is considered as due to general losses, due to the small quantity of material used, the following suggestions as to the true composition of mackintoshite, may be made.

A comparison of the two analyses with that of thoro-gummite shows at once that the change has essentially been the further oxidation of the uranium (from UO<sub>2</sub> to UO<sub>3</sub>) and the assumption of one molecule more of water. Thus, as  $3SiO_2$ ,  $UO_3$ ,  $3ThO_2$ ,  $6H_2O$  expresses well the composition of thorogummite, so  $3SiO_2$ ,  $UO_2$ ,  $3ThO_2$ ,  $3H_2O$  is very probably the formula of the new mineral. In both minerals about one fourth of the thoria is replaced by its equivalent in RO, RO<sub>2</sub>,  $R_2O_3$  which, if later proved to be a constant factor, should be expressed in the formula. Both the analyses seem to show that  $3SiO_2$ ,  $UO_2$ ,  $3(\frac{3}{4}ThO_2, \frac{1}{4}RO)3H_2O$  expresses best the mineral analyzed.

That an anhydrous form occurs in nature, as is thought true of thorite, seems indeed most probable, this would then be  $3SiO_2$ ,  $UO_2$ ,  $3ThO_2$ ; which requires: Thoria 63.67 per cent, silica 14.47 per cent, uranous-oxide 21.86 per cent = 100. As a basic silicate, in condensed form, it could be expressed thus: 3Si,  $4(U, 3Th)O_{14}$ .

In the calculations of the molecular ratios the alkalies and magnesia have been neglected as non-essential and the phosphoric acid has been considered as combined with the excess of uranium; this gives the following results.

	Per cent.	Mol. wt.	Molec. ratios.	
$SiO_2$	$= 13.90 \div$	60 =	23.167 = 3.048 =	3
$UO_2$	22.40	272	8.231 1.083	1
$\mathrm{Th}\tilde{\mathrm{O}}_{2}$	45.30	264	17.159 2.256	
(Yt, La) <sub>2</sub> O <sub>3</sub>	1.86	288	.645	> 3
$ZrO_2$	0.88	122	.721	> D
PbO	3.74	222	1.684 5 700 0.750	
FeO	1.12	72	1 597	
CaO	0.59	56	1·053 j	
$H_2O$	4.31	18	23.944 3.150	3

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The above ratios are as close as could reasonably be expected. It will be interesting to compare the molecular ratios of the theoretical mineral with those found for the analyses of mackintoshite and thoro-gummite and to notice the sharp relationships brought out.

Mackintoshite.					
	Molec.	Molec.			
Theory.	ratio.	Found. ratio. Error.			
$3SiO_2 = 13.87\%$	= 23.11	13.90% = 23.16 = +0.03%			
$1 UO_2 20.95$	7.70	22.40 $8.23$ $+1.45$			
$3 \text{ThO}_2 = 61.02$	23.11	60.35 $22.86$ $-0.67$			
$3 H_2 O 4.16$	23.11	4.31 $23.94$ $+0.15$			

#### Thoro-gummite.

		Molec.		Molec.	
Theory	7.	ratio.	Found.	ratio.	Error.
$3SiO_2 =$	13.16% ==	21.93	13.08% =	21.81 =	-0.08%
$1UO_3$	21.05	7.31	22.43	7.47	+1.38
$3 ThO_2$	57.89	21.92	57.60	21.82	-0.53
$6H_2O$	7.90	43.83	7.88	43.77	-0.05

In conclusion I wish to reiterate the purely conjectural character of the above tabulated results and to repeat the wish of Dr. Hillebrand that more of this new mineral may be found so that its true composition and formula may be known beyond all question or doubt. That the mineral is more basic than either thorite or uranothorite\* seems at once obvious.

I propose the name of mackintoshite for this new species in honor of the able chemist, the late Mr. James Buckton Mackintosh of New York City. The name seems peculiarly appropriate because of the large amount of valuable work which he did in mineralogy and especially since the mineral contained an earth—thoria—to which he had given an especial study.

\*Lindström's analysis of uranothorite gives, by calculation, the ratios of 1:1:2. for silica, bases and water and shows no apparent ratio for the uranium to the other bases.

# ART. XIV.—Alnoite containing an uncommon Variety of Melilite; by C. H. SMYTH, Jr.

In an earlier paper\* the writer described a small dike occurring in a fault fissure at Manheim, N.Y. The rock examined was much decomposed, but showed under the microscope abundant olivine, dark brown mica, magnetite, and perofskite, with considerable quantities of alteration products. Upon this mineralogical composition was based a determination of the rock as peridotite. Some sections showed, in addition to the minerals named, another constituent, "of imperfect lath shape," in color white, green or brown, and with a marked fibrous structure perpendicular to the longer axis. The structure in some of the laths resembled the peg structure of melilite, and suggested that they might belong to this species; but their optical properties, notably the yielding of second order interference colors, seemed to preclude the acceptance of such a supposition.

Recently, however, some sections have been prepared from fresher material, and these show that this first supposition in regard to the nature of the mineral was correct. It is melilite, though in one respect quite different from that mineral as usually described.

In the fresh material the laths are much more abundant than in the altered rock, and possess a more definite and uniform character. Instead of the fibrous structure they show a very perfect peg structure, while the optical properties, with a single marked exception, agree closely with those generally ascribed to melilite. On the other hand, in the weathered rock from which the first sections were made the melilite is so greatly altered that it gives very imperfect evidence of its original character. These sections afford a good illustration of the rule stated by Stelzner+ in regard to other rocks of a similar character: the melilite is often completely decomposed while the olivine remains quite fresh. Adams, 2 also, has stated that in the alnoite of Ste. Anne, Canada, "the melilite is well seen only in sections of the fresh rock," being no longer easily recognizable "when the rock is decomposed to any considerable extent."

\*A Third Occurrence of Peridotite in Central New York, this Journal, III, xliii, p. 322.

† Stelzner, A.: Ueber Melilith und Melilithbasalte, Neues Jahrbuch für Mine-

ralogie, etc., Beilage-Band II, p. 388.
 ‡ Adams, F. D.: On a Melilite-bearing Rock (Alnoite) from Ste. Anne de Bellevue, near Montreal, Canada; this Journal, III, xliii, p. 278.

In the fresh rock the laths show much variation in size, averaging perhaps about 25<sup>mm</sup> in length, but often reaching <sup>5mm</sup>. Their outline is sometimes irregular, sometimes sharply rectangular. Basal sections of the mineral are not common; when seen they usually have an imperfect quadratic shape. The most conspicuous feature of the laths is the peg structure, consisting of small peg-like bodies, usually starting from the basal planes, and extending partly or wholly across the lath. This structure is very unevenly distributed, being quite absent in some cases, and in others extending through the entire lath. Again, it may be confined to one-half of a lath, while the other half is quite free. Sometimes the pegs lie in the central portion of the lath, and do not extend to either face; they may also be elongated parallel to the long axis of the lath. As a rule the outline of the pegs is rather irregular, though it not uncommonly approaches the sharpness and symmetry of Stelzner's figures.\* In the course of alteration the peg structure becomes obscured by the development of a fibrous structure, and the outlines of the laths lose sharpness, quickly destroying the characteristic appearance of the mineral.

Many laths show no trace of cleavage, but in others it manifests itself by a single crack parallel to the long axis. Less often two or more cracks appear. In the earlier stages of decomposition the cracks are sometimes accentuated by the formation of alteration products.

In the thinnest parts of sections the melilite is colorless, elsewhere it has a decided yellowish tint. Compared with melilite from other localities its mean index of refraction is perhaps a little lower, while the double refraction is rather stronger, a yellow interference color being obtained in moderately thin sections. But while differing very slightly from other melilites in these respects, it shows a marked divergence in another property. Examination of the laths with a gypsum plate shows that their long axis is the direction of greatest elasticity, and the short axis the direction of least elasticity. As the mineral is tabular parallel to the basal pinacoid, this gives for its optical orientation a = a and  $\dot{c} = c$ ,  $\omega < \varepsilon$  and the mineral is positive. While this is true of a large proportion of the melilite, it is not invariably the case, for laths are occasionally found in which the mineral is negative. More common is the occurrence of laths, which, though consisting chiefly of positive material, have patches of a negative character scattered through them.

The negative character of melilite as a rock constituent has been so generally regarded as constant that any exception to

\* Op. cit., Taf. VIII, fig. 4.

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the rule is of particular interest. Artificial melilite of positive character has been described by Vogt\* and by Bodländer ;+ but even so recent a work as the third edition of Rosenbusch's "Mikroskopische Physiographie der petrographisch wichtigen Mineralien," though implying the probable existence of a positive molecule in ordinary melilite, does not definitely state that the mineral is sometimes positive in rocks. As a rock constituent melilite of a positive character has been mentioned, so far as the writer knows, only by Becke.<sup>‡</sup> He refers to two nepheline basalts containing melilite of positive character; and as an explanation states that "man wird nicht fehlgehen, wenn mann annimmt, das die gesteinbildenden Melilithe isomorphe Mischungen von zwei Endgliedern seien, von denen das eine mit negativer Doppelbrechung wohl im vesuvischen Humboldtilith vorliegt, während das positive noch unbekannt ist." This explanation is in accord with the facts observed in the Manheim rocks, as well as with the observations of Vogt, who was led to a similar conclusion in regard to the artificial melilite. Bodländer, however, holds that this view is inconsistent with the results of analyses of artificial melilite, and concludes that the mineral is positive when it contains a large amount of magnesium.§

With the view of obtaining further evidence as to the occurrence of positive melilite, sections of, five other rocks containing the mineral have been carefully examined. The rocks are melilite basalts from Wartenberg, Bohemia, and Hochbohl, Württemberg; leucitite from Capo di Bove, Italy; and alnoites from Alnö, Sweden, and Ste. Anne, Canada. All of these localities with the exception of the last, are so noted as to be almost classic. The sections of the first three rocks were prepared by Voigt and Hochgesang in Göttingen. For the sections of the two alnoites, as well as for other assistance, the writer is indebted to Professor George H. Williams.

While in all of these rocks the ordinary negative melilite predominates, in two of them, the melilite basalt from Wartenberg and the alnoite from Alnö, the positive variety exists to some extent. In both rocks it forms entire laths like those in the Manheim rock, being particularly abundant in the basalt.

Although, of course, it does not follow that in an examination of a larger number of rocks as great a proportion would

\* Vogt, J. H. L.: Studier over Slagger, Stockholm, 1884; also Beiträge zur Kenntniss der Gesetze der Mineralbildung in Schmelzmassen und in den neovulkanischen Ergussgesteine, Christiania, 1891.

+ Bodländer, G.: Entstehung von Melilith beim Brennen von Portland-cement,

Neues Jahrbuch für Mineralogie, etc., 1892, I, p. 53. ‡ Becke, F.: Optischer Charakter des Melilith als Gesteinsgemengtheil, Tschermak's Mittheilungen, xii, p. 444.

§ Op. cit. p. 56.

be found to contain positive melilite, still it is probable that this variety of the mineral has a greater distribution than has heretofore been supposed. Its occurrence in such abundance in the Manheim dike adds interest to a rock in itself so rare as to be worthy of special note.

Of the other minerals in the rock the olivine, magnetite, and perofskite show no unusual features and require no description other than that previously given.

The mica, on examination in convergent light, proved to be biotite. In view of the nature of the rock this result was hardly to be expected, and it is probable that anomite is also present, though not yet identified.

Upon the basis of its mineralogical composition, and from a comparison with a specimen from the type locality<sup>\*</sup> the rock must be classed as alnoite. The only respect in which it differs very markedly from the rock at Alnö is in the almost complete absence of pyroxene. With this exception, sections from the two localities are nearly identical in appearance.

The same difference exists in greater degree between the Manheim rock and the one other melilite rock thus far described from this country—the alnoite of Ste. Anne, Canada. The latter rock also contains nepheline which has not been found in the Manheim alnoite. Still, in spite of these differences, the rocks are so closely related that there can be no error in classing them together.

Hamilton College, Clinton, N. Y., April, 1893.

ART. XV.—On Canfieldite a new Germanium Mineral and on the Chemical Composition of Argyrodite; by SAMUEL L. PENFIELD.

It is with great pleasure that the author is able to announce the discovery of a new mineral containing germanium and to record the occurrence of this rare and interesting element from a new locality. The credit of this is due in great measure to the keen mineralogical interest of Mr. Frederick A. Canfield of Dover, N. J., to whom, while on a business trip in Bolivia, South America, some specimens of this mineral were given as samples of a rich and unknown silver ore, by friends connected with the mining industry. These were brought to the writer for identification and he takes great pleasure here in acknowledging his indebtedness to Mr. Canfield and in expressing his

\*Törnebohm, A. E.: Melilitbasalt fraan Alnö; Geol. Fören i Stockholm Förhandl., 1882, vi, No. 76, p. 240.

thanks to him for the liberality with which he has placed an abundant supply of this valuable material at his disposal. It is in acknowledgment of these services that the mineral has been named after him.

It is unfortunate that at the present no further information can be given concerning the exact locality and mode of occurrence, but from inquiries that have been set on foot by Mr. Canfield it is hoped that full data concerning these points will be given later.

When the mineral was brought to the writer, attempts made to identify it at once showed that it was not one of the ordinary silver minerals. Thus in the open tube it gave a reaction for sulphur but no sublimate. In the closed tube with a Bunsen burner flame only a slight sublimate of sulphur, but at a higher temperature with a blowpipe flame the sulphur increased, while nearer the assay a pale yellow sublimate formed, which became lighter on cooling. On examining this with a lens it was found to consist of minute globules most of which were nearly colorless but some were yellow. Boiling concentrated nitric acid was found to attack and oxidize the mineral very slowly. On charcoal in the oxidizing flame it fused readily and gave almost immediately a pure white sublimate near the assay, but no color to the flame. On continued blowing this sublimate moved farther out, assuming a color which varied from greenish to brownish yellow, for the most part lemon yellow, while the assay changed to a pure silver bead. On examining the coating more minutely with a lens it was seen to have a peculiar smooth appearance, as if it had fused on the surface of the charcoal, while scattered about nearer the assay were numerous small transparent to milk white globules, along with minute globules of silver. These tests led to the suspicion that the mineral might possibly contain germanium and a comparative test, made with argyrodite on charcoal, gave exactly the same results. It is to be noted here that while Richter\* describes very minutely the reactions which argyrodite gives on charcoal he does not mention the smooth surface of the coating or the formation of the fused globules which form so characteristic and useful a test for the identification of germanium. In order to prove beyond all doubt the identity of the element thus indicated with germanium the properties of the element as given by Winkler<sup>+</sup> were studied, a series of careful qualitative tests were made together with the formation of most of the important compounds mentioned by him. Thus a sulpho-salt, soluble in alkaline solutions like those of the tin, arsenic and antimony group, was prepared,

> \* Quoted by Weisbach, Jahrb. f. Min., 1886, ii, p. 67. + Journ. f. prakt. Chem., xxxiv, 1886, p. 177.

from which solution the addition of acid, especially in large excess, precipitated a white sulphide. On heating some of this sulphide in a tube through which a current of hydrogen was passed, small glittering scales of GeS, in luster resembling hematite, were formed just beyond the ignited material. These on examination with the microscope in transmitted light were found to be dark brown in color. Although not mentioned by Weisbach<sup>\*</sup> it was noted that these were strongly pleochroic, the direction of greatest absorption being at right angles to the longest axis of the plates. By continued and higher heating a still further reduction took place and metallic germanium was deposited as a crystalline sublimate on the walls of the tube. Microscopic examination showed this sublimate to consist of small gray-white octahedral crystals of magnificent metallic luster. They were found to be insoluble in hydrochloric acid but were readily dissolved by aqua regia. These results agree exactly with those given by Winkler and the identity was still further confirmed by the entire behavior of the element and by other results which will be given in the course of this article.

The physical properties of this new mineral are as follows: Crystallization isometric. Among the specimens furnished by Mr. Canfield were two which were well crystallized. One of these consisted of a group of unmistakable octahedral crystals, averaging about  $7^{mm}$  in axial diameter, but which were too rough for measurement on the goniometer. Their edges were sometimes truncated by the dodecahedron, while some were twinned about an octahedral face. The other specimen contained equally large but less isolated crystals, the luster of whose faces was good and one of the crystals, showing the four upper faces of an octahedron, with edges truncated by the dodecahedron was measured on the reflecting goniometer as follows:

$111 \land 111 = 70^{\circ}$	0'		
$\overline{1}11 \wedge \overline{1}\overline{1}1 = 70$	29		
$\overline{1}\overline{1}1 \land 1\overline{1}1 = 70$	14	$111 \land \overline{1}\overline{1}1 =$	$108^{\circ} 57'$
$1\bar{1}1 \land 111 = 70$	8	$1\bar{1}1 \wedge \bar{1}11 =$	109 3
Calculated, 70	32	Calculated,	109 28

The reflections of the signal were moderately good and considering a slight rounding of the faces the measurements agree as closely to those of the octahedron as could be expected. The dodecahedral faces were too uneven to yield a distinct reflection. These crystals were tested and found to give the characteristic reactions for germanium. The fracture is irregular to small conchoidal. Extremely brittle. Hardness about 2.5. The specific gravity of two distinct, massive fragments,

\* Quoted by Winkler, loc. cit., p. 215.

weighing about five and six grams each, carefully taken on a chemical balance after boiling in distilled water, was found to be 6.2662 and 6.2657 respectively, the temperature being  $25^{\circ}$ C. The specific gravity of the fragment containing the crystal that was measured and weighing over 22 grams was found to be 6.270. The luster is brilliant metallic. The color black with a blueish to purplish tone. The streak is gravish black. The chief pyrognostic properties have somewhat shiny. already been given. In addition the fusibility at about  $1\frac{1}{2}$  to 2 should be noted. The fused transparent globules which were observed on charcoal are probably GeO<sub>2</sub>. Some of the oxide separated from the quantitative analysis was tested on charcoal as follows: In the oxidizing flame it fused with bubbling to a transparent, glassy globule, giving no coating. By continued heating in the reducing flame it darkened and gave slowly a pure white sublimate. The yellow coating obtained on charcoal from the mineral was probably a mixture of oxide and sulphide of germanium. The fused globules, which were observed near the assay in the closed tube are GeS, or possibly some oxysulphide. Argyrodite, when tested in the closed tube, gives at first a black sublimate, which as stated by Richter,\* looks exactly like mercuric sulphide and undoubt-edly is that substance. On intense heating before the blowpipe there formed farthest up on the tube a sublimate of sulphur, next followed the black ring of mercuric sulphide, neither of which increased perceptibly by continued heating, while nearest the assay the nearly colorless globules of GeS, were deposited. On breaking off the lower end of the tube, driving off the sulphur and mercuric sulphide by gentle heat and then roasting the globules in a current of air, SO, was given off while the germanium oxide collected into a fused mass but was not volatilized. Regarding the association of canfieldite with other minerals, all that can be said is that the specimens are remarkably pure, only slight quantities of pyrite, sphalerite and kaolin being attached to them.

It having been shown that the mineral was essentially a sulpho-salt of germanium and silver, the following method was adopted for analysis. A weighed quantity, about two grams, was oxidized by concentrated nitric acid, the operation requiring from one to two hours on the water bath. After the oxidation was complete the excess of nitric acid was removed by evaporation. The residue was then dissolved in warm water slightly acidified with nitric acid, and after filtering off a slight trace of insoluble residue the silver was precipitated by hydrochloric acid, filtered and weighed. In the

\* Quoted by Weisbach and Winkler. Loc. cit.

filtrate the sulphur was precipitated as barium sulphate, which was purified by fusion with sodium carbonate, reprecipitated and weighed. For the determination of germanium another portion of two grams was oxidized by nitric acid with the addition of a little sulphuric acid. After removal of the large excess of nitric acid by evaporation, the residue was dissolved in warm water, with addition of some nitric acid if necessary, the silver precipitated with ammonium thiocvanate and removed by filtration. The filtrate contained the germanium together with no acid which forms with it a volatile compound. It was evaporated in a platinum dish, the nitric acid present serving to completely destroy the ammonium thiocyanate, and the excess of sulphuric acid was finally driven off by heating. The residue thus obtained was covered with a little strong ammonia into which hydrogen sulphide was conducted. Under this treatment the germanium oxide dissolved, while all heavy metals, except those which form sulpho-salts soluble in ammonium sulphide, were left undissolved. In this particular case a very small quantity of a black sulphide remained; it was filtered off, ignited and weighed. It is assumed to be a mixture of zinc and iron oxides, resulting probably from admixed sphalerite and pyrite. The filtrate containing the germanium was collected in a weighed platinum crucible and evaporated on the water bath. The residue was oxidized by strong nitric acid, the excess of which was removed by evaporation. The crucible, placed inside of a porcelain one, was then ignited, gently at first, finally to the full extent of a ring burner, then weighed and the germanium determined as GeO<sub>2</sub>. On further ignition the weight was found to be constant, nor did it change by heating to full redness. When heated in a current of ammonia and air, to remove sulphuric acid, the weight diminished very little; thus in one experiment it fell from 0.1535 to 0.1525 grs., showing that a gentle ignition is sufficient to practically expel all of the sulphuric acid. By heating to a bright redness in a current of ammonia and air the germanium oxide suffered reduction to the metallic state. To show that the germanium oxide was pure and especially to prove the absence of arsenic and antimony the following tests that were made may be mentioned. Rather large quantities of the mineral, when roasted in the open tube gave no sublimate. An acid solution of the oxide gave upon addition of hydrogen sulphide a white precipitate, which when collected on a filter showed only a pale tinge of yellow. Also the oxide obtained in the analysis when dissolved and brought into a Marsh apparatus gave only a most minute and unweighable blackening on the walls of the tube, which on ignition in the air changed to a scarcely perceptible white oxide resembling

antimony. As the mineral dissolves completely in nitric acid tin cannot be present. These results therefore showed that the germanium was satisfactorily pure. Another method of analysis in which everything was determined in one portion is as follows: Solution of the mineral in nitric acid, precipitation of the silver with hydrochloric acid, of the sulphur with barium nitrate, removal of the excess of chlorine and barium in one operation with silver nitrate and sulphuric acid, final removal of the silver by ammonium thiocyanate and determination of the germanium in the filtrate as above.

• The result of the analysis gave the following figures :

				Average.	Deducting impurities.	Theory for $Ag_8GeS_6$
S	17.03	17.04		17.04	17.10	17.06
Ge	6.51	6.52	6.61	6.55	6.57	6.42
Ag	76.01	76.09		76.05	76.33	76.52
Fe, Zn	•14	·16	•10	·13		
Insol	•29			•29		
				100.06	100.00	100.00

The formula of the mineral is evidently  $Ag_sGeS_c$  or  $4Ag_2S$ .  $GeS_2$ . The agreement of the analysis with the theory as will be noticed is reasonably close.

Winkler made the following analysis of argyrodite, from which he derived the formula Ag<sub>6</sub>GeS<sub>5</sub> or 3Ag<sub>2</sub>S. GeS<sub>5</sub>.

Analysis by Winkler.	Theory for Ag <sub>6</sub> Ge <sub>5</sub> S <sub>5</sub>	Theory for Ag <sub>8</sub> GeS <sub>6</sub>	Atomic weights
S 17.13	18.21	17.06	32
Ge 6.93	8.23	6.42	72.32
Ag 74.72	73.56	76.52	107.7
Hg ·31			
Fe66			
Zn ·22			
99.97	100.00	100.00	

It will be noticed that Winkler's analysis agrees much more closely with the theory for  $Ag_8GeS_{e^1}$  especially in respect to the sulphur and germanium, than with the formula advanced by him. It seems probable, therefore, that the two minerals have the same chemical composition, but since Weisbach has shown that argyrodite is monoclinic and since canfieldite is isometric, they cannot be identical.

In order to investigate this point more closely it seemed desirable to make a new analysis of argyrodite by the same methods which had been used for canfieldite. The material was very carefully selected from an excellent specimen of the

Freiberg argyrodite in the collection of Prof. Brush. The specific gravity was determined in two ways. Some larger fragments, weighing about two grams, gave on the chemical balance in distilled water 6.149 and the smaller ones gave by use of the pycnometer 6.162. These results, though somewhat higher than those given by Winkler and Weisbach, which were 6.085-6.111, are still considerably lower than the specific gravity of canfieldite. The result of the analysis is as follows:

			Average.
S	16.97		16.97
Ge	6.67	6.62	6.64
Ag	75.57	75.53	75.55
Hg	•34		•34
Fe, Zn	•24		•24
			99.74

It will be seen that this analysis agrees remarkably well with that of Winkler, the only essential difference being that the silver is somewhat higher and the iron and zinc are lower. This suggests that these latter are impurities, resulting from the presence of a slight admixture of pyrite and sphalerite, both of which are associated with the mineral. In regard to the mercury, since this element has never been known to occur otherwise at Freiberg, it is probable that it replaces silver. If we now recalculate these analyses, excluding the iron and zinc with sufficient sulphur to form pyrite and sphalerite, and replacing the mercury by its equivalent in silver, we obtain the following:

Canfieldite.	Argyrodite, Winkler.	Argyrodite, Author.	Theory for Ag₅GeS₅
17.10	16.56	16.83	17.06
6.57	7.05	6.69	6.42
76.33	76.39	76.48	76.52
100.00	100.00	100.00	100.00

From the consideration of these results there can be no doubt that canfieldite and argyrodite have the same chemical composition, which is  $Ag_sGeS_e$ . It is evident therefore that we have here a case of dimorphism, for both the crystalline forms and the specific gravities indicate that the minerals are distinct.

Laboratory of Mineralogy and Petrography, Sheffield Scientific School, June, 1893.

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, NO. 272.-AUGUST, 1893.

# ART. XVI.— Epeirogenic Movements associated with Glaciation; by WARREN UPHAM.

GEOLOGY is indebted to Gilbert in his monograph, "Lake Bonneville," for the terms epeirogeny and epeirogenic, designating the broad movements of uplift and subsidence which affect the whole or large portions of continental areas or of the oceanic basins. These terms are distinguished from orogeny and orogenic, which denote the folding, faulting, and upheaval of limited tracts as mountains and mountain ranges, forming narrow belts as compared with the extensive plateaus of the Epeirogenic uplifts and depressions, except in continents. areas of contemporaneous orogenic disturbance, take place apparently by gentle monoclinal or quaquaversal tilting of the marginal or outer parts of the broad regions affected, and exhibit a very gradual change in altitude from the central parts of those regions to the undisturbed surrounding areas. In the region of Lake Agassiz and of the Laurentian lakes, whose epeirogenic elevation after the recession of the ice-sheet has been well ascertained in its southern part by levelling and is found to vary from a few inches to somewhat more than five feet per mile of differential uplift from south to north, the movement has been so gradual that the continuity of the glacial lake beaches remains perfect, with no dislocations to indicate any faulting of the underlying bed-rocks.

Especial interest pertains to the epeirogenic movements of the Quaternary era from their relationship to the accumulation and departure of the Pleistocene ice-sheets, which was first pointed out by Dana in his presidential address before the American Association in 1855, as published in this Journal the following year. By reasoning from the prevalence of fjords in all glaciated regions and showing that these are valleys eroded by streams during a formerly greater elevation of the land previous to glaciation, and from the marine beds of the St. Lawrence valley and basin of Lake Champlain belonging to the time immediately following the glaciation, it was announced that the formation of the drift on this continent was attended by three great continental movements: the first upward, during which the ice-sheet was accumulated on the land; the second downward when the ice-sheet was melted away, and the third, within recent time, a re-elevation, bringing the land to its present height. With the moderate depths of the fjords and submarine valleys then known, the amount of preglacial elevation which could be thus affirmed was evidently too little to be an adequate cause for the cold and snowy climate pro-

ducing the ice-sheet. The belief that this uplift was 3,000 feet or more, giving sufficiently cool climate, as Prof. T. G. Bonney has shown, to cause the ice accumulation, has been only reached within the past few years by Spencer, LeConte, Hilgard, and the present writer, through the discoveries by soundings of the U.S. Coast Survey, that on both our Atlantic and Pacific coasts submarine valleys evidently eroded in late Tertiary and Quaternary time reach to profound depths, 2,000 to 3,000 feet below the present sea level.\*

Although the adequacy of the preglacial epeirogenic uplift of this continent to produce its Pleistocene ice-sheet was tardily recognized and cannot yet be said to be accepted by all American glacialists, it was distinctly claimed by Dana in 1870 that the Champlain subsidence of the land beneath its iceload, supposing it to have been previously at a high altitude, must have brought climatic conditions under which the ice would very rapidly disappear. The depression would be like coming from Greenland to southern Canada and New England. In Professor Dana's words: "Such an extended change of climate over the glacier area was equivalent in effect to a transfer from a cold icy region to that of a temperate climate and melting sun. The melting would therefore have gone forward over vast surfaces at once, wide in latitude as well as longitude."+

Such explanations as these accounting for the gradual accumulation and comparatively rapid dissolution of the North American ice-sheet are also found to be applicable to the icesheets of other regions. The fjords of the northern portions of the British Isles and of Scandinavia show that the driftbearing northwestern part of Europe stood in preglacial time 1,000 to 4,000 feet higher than now, while on the other hand late glacial marine beds and strand lines of sea erosion testify that when the ice disappeared the land on which it had lain was depressed 100 to 600 feet below its present height, or nearly to the same amount as the Champlain depression in North America. Again, just the same evidences of abundant and deep fjords and of marine beds overlying the glacial drift to heights of several hundred feet above the sea are found in. Patagonia, as described by Darwin and Agassiz. On these three continental areas, the widely separated chief drift-bearing regions of the earth are found to have experienced in connection with their glaciation in each case three great epeirogenic movements of similar character and sequence, first, a

<sup>\*</sup> Detailed notes of these submerged valleys are presented in my payer "On the

Cause of the Glacial Period," Am. Geologist, vol. vi, pp. 327-339, Dec., 1890. † Trans. Conn. Acad. of Arts and Sciences, vol. ii, 1870, p. 67. Compare this Journal, III, vol. x, pp. 168-183, Sept., 1875.

great and comparatively long continued uplift, which in its culmination appears to have given a high plateau climate with abundant snowfall forming an ice-sheet, whose duration extended until the land sank somewhat lower than now, leading to amelioration of the climate and the departure of the ice, followed by re-elevation to the present level. The coincidence of these great earth movements with glaciation naturally leads to the conviction that they were the direct and sufficient cause of the ice-sheets and of their disappearance; and this conclusion is confirmed by the insufficiency and failure of the two other chief theories which have been advanced to account for the Glacial period.

During ten or fifteen years next following the publication of Dr. James Croll's very valuable work, "Climate and Time," and of the equally grand work by Prof. James Geikie, "The Great Ice Age," a quite general opinion among American glacialists favored the astronomical theory of the causes of glaciation which these authors so ably advocated. But in later years a similarly general opinion among us sets against that theory because of the uniqueness and the demonstrated geologic recency of the Glacial period; and therefore for a time some, who were specially impressed with the low level of our continent during the maximum and wane of its glaciation, looked with careful inquiry toward the doctrine of changes in latitude and in the position of the earth's poles, which was set forth in 1866 by Sir John Evans, with the suggestion that it might explain the remarkable Pleistocene changes of climate. Within the past two years, however, the brilliant discoveries by Dr. S. C. Chandler\* of the periods and amounts of the observed variations of latitude, showing them to be in two cycles respectively of twelve and fourteen months, with no appreciable secular change, forbid reliance on this condition as a cause, or even as an element among the causes, of the Ice age. The second of these theories is out of the field, and the first, even in the modified form given to it by Wallace in "Island Life," cannot be admitted, in the opinion of most American students of this subject, when we find that the Ice .age ended probably only 6,000 to 10,000 years ago.

The epeirogenic movements of the countries which became glaciated were only a portion of wide-spread oscillations of continental areas during the closing part of Tertiary time and the ensuing much shorter Quaternary era. Not only was northwestern Europe uplifted thousands of feet, but probably all the western side of Europe and Africa shared in this movement, of which we have the most convincing proof in the

\* Astronomical Journal, vol. xii, pp. 57-62, 65-72, and 97-101, Aug. 4 and 23, and Nov. 4, 1892.

submerged channel of the Congo, about four hundred miles south of the equator. From soundings for the selection of a route for a submarine cable to connect commercial stations on the African coast, Mr. J. Y. Buchanan\* found this channel to extend eighty miles into the ocean to a depth of more than 6,000 feet. The last twenty miles of the Congo have a depth from 900 to 1,450 feet. At the mouth of the river its width is three miles and its depth 2,000 feet. Thirty-five miles off shore the width of the submerged channel or cañon is six miles, with a depth of about 3,450 feet, its bottom being nearly 3,000 feet below the sea bed on each side. Fifty miles from the mouth of the river the sounding to the submarine continental slope is nearly 3,000 feet, while the bottom of the old channel lies at 6,000 feet. This very remarkable continuation of the Congo valley far beneath the sea level is like those of the Hudson and St. Lawrence rivers, and like numerous submerged valleys on the coast of California; but the Congo reaches to a greater depth than these of North America, and even exceeds the Sogne fjord, the longest and deepest in Norway, which has a maximum sounding of 4,080 feet. Another deep submarine valley, called the "Bottomless Pit," having soundings of 2,700 feet, is described by Buchanan on the African coast 350 miles north of the equator, and he states that a similar valley exists in the southern part of the Bay of Biscay. These observations show that within very late geologic time probably almost the entire Atlantic side of the eastern continent has been greatly uplifted, attaining as high an altitude as that which A. C. Ramsay and James Geikie conjectured as a possible cause of the frost-riven limestone agglomerates of Gibraltar.+

Likewise the tropical portions of the western continent, the West Indies, and the smaller islands of the Caribbean region, appear to have shared the epeirogenic disturbances which were associated with the glaciation of the northern and southern parts of this continent, as is well brought out by the recent studies and discussions of the geology of Barbados island by A. J. Jukes-Browne and J. B. Harrison, ‡ and by the close relationship of the Pacific and West Indian deep sea faunas on the opposite sides of the Isthmus of Panama, made known through dredging by Alexander Agassiz.§ This testimony, indeed, with that of Darwin, L. and A. Agassiz, and others, of very recent, extensive, and deep subsidence of the western

<sup>\*</sup> Scottish Geographical Magazine, vol. iii. 1887, pp. 217-238.

<sup>†</sup> Quart. Jour. Geol. Soc., vol. xxxiv, 1878, pp. 505-541. † Quart. Jour. Geol. Soc., vol. xlvii, 1891, pp. 197-250. § Bulletin Mus. Comp. Zool. at Harvard College, vol. xxi, pp. 185-200, June, 1891.

coast of South America, apparently however continuing for no long time, lends much probability to the supposition that the low Panama isthmus was somewhat deeply submerged for a geologically short period contemporaneous with epeirogenic uplifts of the circumpolar parts of this continent both at the north and south, whereby the effects of high altitude in covering the northern and southern high areas with ice-sheets were augmented by the passage of much of the Gulf Stream into the.Pacific Ocean.

The end of the Tertiary era and the subsequent Glacial period have been exceptionally characterized by many great oscillations of continental and insular land areas. Where movements of land elevation have taken place in high latitudes, either north or south, which received abundant precipitation of moisture, ice-sheets were formed; and the weight of these ice-sheets, as was first pointed out by Jamieson, seems to have been a chief cause, and often probably the only cause, of the subsidence of these lands and the disappearance of their ice. But the original sources of the energy displayed in the earth-movements of uplift preceding glaciation, and why this has been so extensively developed during the Quaternary era, are very difficult questions which it is not the purpose of this paper to consider, since I have attempted elsewhere to answer them, in an appendix of Wright's "Ice Age in North America" It may be properly noted, however, that the explanations mentioned are entirely consistent with Dana's teaching that the great continental and oceanic areas have been mainly permanent from very early geologic times.

Two formidable objections to this view that the accumulation of the Pleistocene ice-sheets was preceded and caused by great epeirogenic elevation deserve careful attention. The first consists in an approximate identity of level with that of to-day having been held by many drift-bearing areas at a time very shortly preceding their glaciation. This is clearly known to have been true of Great Britain and of New England. Near Boston, for example, my observations of fragments of marine shells in the till of drumlins in or adjoining the harbor prove for that tract a preglacial height closely the same as now at so late a time that the molluscan fauna, of which we have a considerable representation, comprised only species now living. In respect to this objection, it must be acknowledged that the preglacial high elevation which I think these areas experienced was geologically very short. With the steep gradients of the Hudson, of the streams which formed the now submerged channels on the Californian coast, and of the Congo, these rivers, if allowed a long time for erosion must have formed even longer and broader valleys than the still

very impressive troughs which are now found on these submarine continental slopes. But the duration of the epeirogenic uplift of these areas on the border of the glaciation for the Hudson, beyond it for the Californian rivers, and near the equator in western Africa, can scarcely be compared in its brevity with the prolonged high altitude held during late Tertiary and early Quaternary time by the Scandinavian peninsula and by all the northern coasts of North America from Maine and Puget Sound to the great Arctic archipelago and Green. The abundant long and branching fjords of these land. northern regions, and the wide and deep channels dividing the many large and small islands north of this continent, attest a very long time of preglacial high elevation there. At the time of culmination of the long continued and slowly increasing uplifts at the north, they seem to have extended during a short epoch far to the south, coincident with the formation of ice-sheets in high latitudes. But when these lands became depressed and the ice burden of the glaciated countries was removed, they in some instances, as in Great Britain and New England, returned very nearly to their original levels beautifully illustrating the natural condition of equilibrium of the earth's crust, which Dutton has named *isostasy*, that when not subjected to special and exceptional stresses it acts as if floating on a heavier plastic and mobile interior.

Somewhat analogous with the foregoing is the second of these objections, namely, the fully proved low altitude of the glaciated lands when the ice-sheets attained their maximum extent and during the diversified and fluctuating history of their recession. It must be recognized, however, that we have in the complex series of drift deposits left for our examination only a representation of the later and closing phase of the Ice age, while the land was low or near its present level. The comparatively much longer early phase of high altitude attending the accumulation and slow extension of the ice-sheets on this continent is not clearly represented by the drift and numerous moraines of the glacial retreat or of the extreme limit of glaciation, but by the earlier fluvial Lafayette formation, in which, according to Hilgard, coarse gravel from the Archæan areas near the head of the Mississippi was carried down by that stream quite to the shores of the Gulf of Mexico. attesting, as he believes, an altitude of the Upper Mississippi region at least 3,000 feet higher than now \*

The wane and departure of both the North American and European ice-sheets have been marked by many stages of halt and oscillation, whereby the flora, including forest trees, and less frequently traces of the fauna, of the temperate areas

\* This Journal, III, vol. xliii, pp. 389-402, 1892.

adjoining the melting and mainly receding ice were covered by its drift at the times of temporary re-advance of the iceborder. No better illustration of conditions favorable for the burial of forest beds in the drift can be imagined than those of the Malaspina glacier or ice-sheet, between Mt. St. Elias and the ocean, explored by Russell in 1890 and 1891 and found to be covered on its attenuated border with drift which supports luxuriant growing forests. Let a century of exceptional snowfall cause a thickening and re-advance of that icesheet, and sections of its drift exposed after the glacial recession will show a thick forest bed of chiefly or wholly temperate species. Such re-advances of the continental ice-sheets, interrupting their retreat, are known by well marked recessional moraines in both North America and Europe. Near the drift boundary in the Mississippi basin some of these glacial fluctuations have involved long stages of time, measured by years or centuries, with important though minor changes in altitude, as shown by the excellent analytic studies of Chamberlin, Salisbury, and Leverett; but farther north, as in the large region of the glacial Lake Agassiz, the withdrawal of the ice-sheet and formation of successive moraines marking slight halts and re-advances due to secular changes in temperature, humidity, and snowfall, were demonstrably very rapid, the whole duration of this glacial lake being probably only about 1,000 years.\* The vicissitudes of the general glacial retreat seem to me to have been due thus chiefly to variations of snowfall, some long terms of years having much snow and prevailingly cool temperature, therefore allowing considerable glacial re-advance, while for the greater part other series of years favored rapid melting and retreat.

Under this view we may, I think, account for all the observations which have been held in America and Europe as proofs of interglacial epochs, without assuming that there was either any far re-advance of the ice-border or any epeirogenic movements attending the glacial retreat of such magnitude as to induce the fluctuations of which the forest beds and marginal moraines bear witness. Though the whole history of the wane of the ice-sheets is indeed very complex and long, as measured by our familiar historical time units, it was yet, in my opinion, geologically very brief, if compared with all preceding geologic periods and epochs. The formerly supposed necessity of predicating long interglacial epochs seems to me a misunderstanding. Instead, as Dana, Wright, Hitchcock, Lamplugh, Kendall, Falsan, Holst, Nikitin, and many other glacialists believe, the Ice age seems to me to have been essentially continuous

\* Geol. and Nat. Hist. Survey of Canada, Annual Report, New series, vol. iv, for 1888-89, p. 51 E.

and single, with important fluctuations, but not of epochal significance, both during its advance and decline.

The Champlain subsidence of the land beneath its ice-sheet probably affected the whole of the preglacially elevated area before the growth of the ice-sheet was checked. For some time the increase in the ice accumulation may have exceeded the rate of depression, so that the surface of the thickening But at ice-sheet continued to hold an undiminished altitude. length the subsidence brought a warmer climate on the southern border of the ice, causing it to retreat, and probably giving to it a mainly steeper frontal gradient than during its growth and culmination. To this steeper gradient and consequently more vigorous glacial currents I attribute the larger morainic accumulations of drift marking retreatal stages than on the outermost drift boundary. When the ice had considerably receded, the outer portion of the depressed area was somewhat uplifted, to approximately its present height, which it has since held, excepting minor oscillations. Gradually, as the ice withdrew from south to north, a principally permanent wave of land elevation has followed, earliest uplifting the loss region of the Mississippi basin, later the areas of Lake Agassiz, of the Laurentian lakes, including Lake Champlain, and of the St. Lawrence valley, and latest the country surrounding Hudson Bay, where this movement is still in progress. The time since the departure of the ice there has been too short, as in Scandinavia, to allow the earth's crust yet to have completed its restoration to an isostatic condition.

# ART. XVII.—On Antennæ and other Appendages of Triarthrus Beckii; by W. D. MATTHEW.

#### [Read before the N. Y. Academy of Sciences, May, 1893.]

AMONG the problems which paleontologists have in vain tried to solve was, till a few years ago, that of the structure and affinities of the trilobite. In all the vast numbers of these animals which have been found and studied, scarcely any parts have been preserved besides the dorsal shield and hypostome. The legs, gills, and such other organs as they may have had, have practically never been shown on any specimen. This is chiefly because of the easy break afforded by the hard, smooth, carapace, but partly also because of the character of these organs, which seem to have been soft, easily disjointed, and prone to maceration and decay. The only cases, so far as I know, in which the organs of the under side have been definitely seen and described, are three specimens of Asaphus platycephalus\*—all found at different times and places—in which a number of legs are preserved in a fragmentary way, another of the same genus showing a palpus† attached to the hypostome, and a few cases in which a detached leg or antenna was found in company with species of trilobites, and referred to one of them. Other discoveries have been reported from time to time, but not conclusively verified.

It has, however, been found possible by cutting thin sections of trilobites especially well preserved, to determine the nature and position of the organs of the under side. Mr. C. D. Walcott<sup>‡</sup> in 1881 published the results of a very successful investigation of this kind, extending over several years, and based on the study of over 2000 thin sections. His article has given us a very complete knowledge of the organization, at least of the two genera Ceraurus and Calymene, which were the subjects of his study.

The structure as thus determined involved :

1. A ventral membrane over the under side of the body, with hardened arches across each segment, bearing the appendages.

2. Cephalic limbs. There were four pairs of these, the last of which was larger and expanded at the terminal joint into a swimming organ. The bases of these limbs were manducatory in their action as in the modern King-crabs.

3. Thoracic and abdominal appendages. One pair of legs was found to be attached to each segment of the thorax and pygidium. On the basal joint of each was a small epipodite, and two branchiæ, which were in the form of narrow spiral ribbons. The legs, like those of the head, were generally composed of six joints, which were more or less conical, the basal end smallest. Other forms of gills were also met with, viz: a straight uncoiled ribbon in immature specimens, and a radiating leafy form found sometimes in the anterior part of the thorax. There is no mention of cephalic gills.

4. No trace of any antennal system was found.

Mr. Walcott concludes that the trilobites were more nearly allied to the Limulids than to any other living form, and should be classed with them and the Eurypterids, but as a separate subclass. As to their habits, he concludes that they probably were free swimming only when young, and crawled around on the bottom, with very limited swimming powers, when mature.

\* Quar. Jour. Geol. Soc., 1870, p. 479; Cincinnati Jour. Nat. Hist, vol. vi, 1883. + Quar. Jour. Geol. Soc., 1870, p. 486.

+ Quar. Jour Geol. Soc., 1870, p. 486. + Bull. No. VIII, Harvard Museum of Nat. Hist. Mr. Walcott gives very complete references and history up to that date, which I have not thought necessary to repeat. Within the past few months Mr. W. S. Valiant has collected a very considerable number of specimens of *Triarthrus Beckii*, in which the organs of the under side are attached to the body and fairly well preserved. They occur in the Hudson River shales\* near Rome, N. Y. A number of the best specimens are now in the Museum of Columbia College, and Prof. Kemp has very kindly given me the privilege of describing them.

The trilobites are found in a soft, fine, black shale and are very perfectly preserved. The most noticeable character about them is the presence of long, many jointed, rod-like attachments to the front of the head, which resemble exactly the antennæ of other crustaceans. These come out close together from just under the center of the anterior border of the headshield, and diverge generally at an angle of 30° or 40°. In one specimen (fig. 1) a length considerably exceeding that of the glabella is shown; + in the rest they are more broken, but a considerable length is preserved in three or four, and the stumps are distinctly seen in upwards of twenty others. They curve slightly outward and taper gradually down toward the end; the tip itself is not preserved. These antennæ are composed of a great number of joints, each of which is conical, about half as long as wide, and smallest at the base. (See fig. 1a.) As preserved in the rock, they are calcareous, but seem to have been of a structure less firm and thick than the substance of the carapace. Their point of origin seems to be under the front part of the glabella, as they can be traced a little way under the headshield, where they almost coalesce, then turn upward and outward and disappear; with no joints in this part, so far as I have been able to follow it. (See fig. 2.) Just over the spot where they come out, the anterior margin is arched slightly upward, seemingly to give room for their play to and fro.

These organs must certainly belong to the trilobite; when attached they are in all cases in exactly the same position, and are but rarely to be seen separate; moreover, in a number of specimens in which they were not shown they were developed by cutting away the matrix in the proper place. Their character seems also tolerably certain, as both in position and structure they are like the antennæ of modern crustaceans. The appearance of the right hand antenna in fig. 3 may indicate that these organs could be bent back under the sides of the head—but this point needs more evidence. Another specimen,

\* Though referred to the Hudson River by Mr. Valiant, Prof. Whitfield is disposed, on palæontological grounds, to consider them as Utica shales.

+ Mr. Valiant has since shown me a specimen which has antennæ one and a half times as long as the glabella. He informs me that there are now about sixty specimens showing antennæ.

belonging to Prof. A. H. Chester, shows an antenna with the end coiled spirally inwards.

Besides these, there are shown in several of the specimens, other appendages, some of which may be branchial in their character, and others walking or swimming legs. In fig. 1 the side of the head-shield has been broken away, exposing the appendages apparently of three cephalic segments. These are of two kinds, one of which is a narrow, jointed cylindrical leg, and the other is thin, broad and leafy, with what seems to be a comb-like structure similar to the gills of many crustacea. These branchiæ, if so they be, depend from a narrow, thickened anterior edge or limb; they seem to correspond with two of the three legs shown in the specimen, and to overlie them. By analogy with Mr. Walcott's determinations, they are probably attached to the basal joint of the legs.

In figs. 2, 3 and 6 are shown the ends of appendages which projected from under the carapace, and seem to belong to the thoracic region. These are likewise of two kinds, one flat, furrowed, and showing a series of oblique parallel lines all along it (see figs. 2,  $2\alpha$ , 3 and 4); and the other a strong tapering leg, with three cylindrical or slightly flaring joints visible (see figs. 2,  $2\alpha$ , 3, 5 and 6). The first may be a branchial appendage; it is flattened and appears in one case to broaden out into a small paddle at the tip (though this may very likely be deceptive); it has a sharp ridge and narrow furrow along the anterior edge, and behind that the series of lines or comblike structure, which may be due to the remains of hairs or gill structure on the limb.

Figure 4 shows a series of appendages of both kinds, but very poorly preserved. In figure 7 the projecting appendages of the tail-piece are shown, and it may be seen that apparently several, and perhaps all of the pygidial limbs are anchylosed, so as to make a rounded flap, which in shape, though not in structure, reminds one of the telson of a crayfish, and may possibly have served somewhat the same purposes.

The conclusions as to the nature of these appendages are only provisional, and may be much changed by further discoveries. They are not nearly as well preserved as the antennæ, nor in so considerable a number of specimens; for besides those figured, there are but two or three others which show them at all, and those only in traces. The shape and structure of the supposed branchiæ, in particular, are very hard to distinguish; the figures given, however, represent as far as I can see the actual outlines preserved.

It will be seen that the structure of Triarthrus must have differed not a little from that described by Mr. Walcott in Calymene and Ceraurus. The presence of antennæ, the peculiar cephalic organs, and the anchylosed flap under the pygidium, would all be important points of difference, and indicate that the Trilobites were quite varied in structure, and probably included several widely differing types. If the classification founded on the characters of the shield is not deceptive, we may perhaps consider that the structure of Triarthrus was that of all the Olenidæ, the family to which it belongs; while many of the later trilobites would come nearer to Calymene and Ceraurus in their structure.

As regards the probable affinities of the trilobite, as modified by Mr. Valiant's discovery, the writer can scarcely venture any remarks, except tentatively. The homology with Limulus seems not to be as close in Triarthrus as in the forms studied by Mr. Walcott; but the characters seem to be of a more comprehensive type, approaching the general structure of the other Crustacea rather than that of any special form. The presence of antennæ need not, one would think, separate them from the Pœcilopoda; for a small pair occurs in Eurypterus, and the anterior pair of appendages in Limulus are thought to be modified antennæ. The cephalic organs are peculiar, if proved to be gills, and though in the solitary specimen showing them they seem to belong to the head, yet farther proof would be desirable that they are not displaced thoracic limbs. The fused pygidial flap may be a less important character, as it might be induced by some change of conditions of life.

As regards the habits of Triarthrus, we may conjecture that it usually scuttled through the soft mud which composed the shale in which it is found, on the little pointed walking legs; but that it had considerable swimming powers, more so perhaps than the later types of trilobites.

It is hardly to be expected that these antennæ, still less the other organs, will be found in specimens of trilobites unless they are exceptionally well preserved. But one character, the arching of the anterior rim at the center of the head—if not a mere accident of preservation in these specimens—may be found to exist in less perfect fossils, and would be a fair indication of the former existence of antennæ which passed under it.

In conclusion, I wish to acknowledge the kindness of Prof. Kemp in allowing me the privilege of describing these speci mens. I have also to thank Prof. Whitfield for advice and assistance which have been very useful to me in the subject.

*Note.*—As regards the supposed gills under the head, it would seem more probable that they were long, thickly set hairs or fimbriæ on a narrow limb, and served as mouth organs rather than gills, though perhaps also assisting in the respiration.

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## ART. XVIII.—On the Reduction of Nitric Acid by Ferrous Salts; by CHARLOTTE F. ROBERTS.

[Contributions from the Kent Chemical Laboratory of Yale College-XXV.]

AMONG the most common methods for the estimation of nitric acid are those which depend upon its reduction by a ferrous salt in acid solution. The amount of the nitrate acted upon is reckoned either from the oxidation of this ferrous compound or from the nitric oxide set free and subsequently determined. The first named method was first put in practical form by Pelouze, and in its present modified form,\* is capable of yielding accurate results in the analysis of pure nitrates. Organic matter interferes, however, with the accuracy of the indications of Pelouze's process. Schloesing† was the first to use the nitric oxide evolved as a measure of the original nitrate. and he was able to show that the presence of organic matter does not influence the yield of nitric oxide in the decomposi-Schloesing originally estimated the nitric oxide by coltion. lection over mercury, re-conversion by the action of oxygen to nitric acid, and titration of the last with standard alkali, but Reichardt, Wildt and Scheibe§ and others have very much simplified the apparatus of the original process, and shown that the gas may be collected over caustic soda or potash without materially diminishing the accuracy of the analytical Schulze and Wulfert determined by direct measureprocess. ment the nitric oxide collected over mercury, and Tiemann showed that the determination loses little in exactness when the gas is measured over an aqueous solution of caustic soda.

Many modifications and extensions of these processes have appeared from time to time, the detailed consideration of which is not essential to the purpose of the present discussion, but all, whether dependent upon the determination of the change of condition of the iron salt in the residue, or upon the estimation of the nitric oxide evolved, rest upon the assumption that under the conditions of action nitric oxide is the sole reduction product in the complete destruction of the nitric acid by the ferrous salt. That this assumption is true in the main is evidenced by the analytical results of the methods. Thus, in his careful and critical examination of methods, Eder¶ found that the indications given by titration of the residue of treatment with ferrous chloride and hydrochloric acid by means of potassium permanganate showed errors of excessive oxidation amounting only to 0.3 per cent to 1 per

‡Zeitschr. für Anal. Chem., ix, 26.

Zeitschr. für Anal. Chem., ix, 400.

<sup>\*</sup> Fresenius, Quant. Anal., 6th Aufl., p. 519.

<sup>†</sup> Ann. de Chemie, III, xl, 479.

<sup>§</sup> Zeitschr. für Anal. Chem., xxiii, 151.

Tzeitschr. für Anal. Chem., xvi, 267.

cent upon amounts approximating 0.4 grms. of potassium nitrate, although the process involved the uncertainties of titrating, without the now used precautions, with permanganate in hydrochloric acid. The similar process in which use is made of ferrous sulphate in sulphuric acid, instead of the chloride in hydrochloric acid, gave excellent results and showed errors of loss of the nitrate ranging from 0.05 per cent to 0.4 per cent upon similar amounts of the nitrate, while Braun's process of determining the oxidized iron by stannous chloride gave upon amounts of the nitrate varying from 0.16 grms. to 0.32 grms. errors of 0.3 per cent to 1.5 per cent.

In the processes involving the treatment of the nitric oxide, the errors are usually greater and more variable. Thus, Schloesing's process gave Eder errors of 0.2 per cent to 2 per cent upon approximately 0.15 grms. of the nitrate, and 10 per cent and 12.5 per cent respectively upon 0.0279 grms. and 0.0249 grms. of the nitrate. In Reichardt's modification the errors are slightly larger on the average but vary similarly, and Tiemann's method of measuring the gas over caustic soda yields results closely comparable with those of the Reichardt process and but little inferior to those of Schloesing.

The way in which the results vary in all the processes in which the nitric oxide is estimated has very generally been regarded as suggestive of an oxidizing action upon the nitric oxide, nearly constant in amount, and productive of increasing percentage errors as the amount of nitrate decreases. The intermixture of ordinary air would naturally produce diminution of the volume of the nitric oxide, but the oxidation of this by free air of normal composition should produce no effect upon the total volume of the gas in cases where this is measured, if the oxidation goes, as is generally supposed, to the point of forming nitrous acid; for the introduction of a given volume of oxygen (in air) means the simultaneous introduction of four volumes of nitrogen, and the single volume of oxygen is capable of causing the disappearance of exactly four volumes of nitric oxide converting it into nitrous acid, so that four volumes of nitrogen would be left to replace the four volumes of nitric oxide removed. If the oxidation be supposed to go to the point of forming some nitric acid there should be left three volumes of nitrogen to replace every volume of nitric oxide converted to nitric acid, and the total volume should be greater after oxidation than before.

In order to account for the low results, therefore, on the assumption of an oxidizing action due to free air, we must conclude that such air is derived principally from solution in the reagents, which would naturally hold oxygen in excess of the proportion in which it exists in atmospheric air. Air in solution in the receivers would most readily produce the ob-AM. JOUR. SCI.—THIRD SERIES, VOL. XLVI, NO. 272.—AUGUST, 1893.

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served decrease in volume, for the nitrogen in dissolved air would naturally still remain dissolved without relation to the disappearance of dissolved oxygen. If the deficiencies observed in Schloesing's process are due at all to oxidation of the nitric oxide, it is natural to suppose that such oxidation must take place during the passage of the gas from the evolution flask to the mercurial receiver, but in the processes which involve the collection of the gas over aqueous caustic alkali oxidation might readily be brought about by dissolved oxygen, and in this case the nitric oxide removed would not be replaced by nitrogen. The last mentioned source of error, Glaser\* has recently proposed to correct by collecting the gas over a solution of potassium iodide instead of over caustic soda.

The deficiency in the total volume of gas may also be caused partially or wholly by the solubility of nitric oxide in caustic Warington<sup>+</sup> has shown that caustic soda is capable of alkali. slowly absorbing nitric oxide, and Russell and Lapraikt state that upon long standing over caustic soda, nitric oxide is decomposed into nitrous acid, nitrous oxide, and nitrogen.

Errors of the same sort and in the same direction as those produced by the action of caustic alkali, either alone or with dissolved air, or of air in the apparatus, would be the natural consequence of a failure of the ferrous salt to effect decomposition exactly according to the assumed reaction. Incompleteness of decomposition of the nitric acid, or the formation of an oxide of nitrogen higher than nitric oxide would result in producing too small a volume of nitric oxide, and so also would the over reduction of the nitric oxide to nitrous oxide or nitrogen. We have, moreover, abundant evidence on the one hand both of the incompleteness of decomposition of nitric acid, and of the production of a higher oxidation product by the action of the ferrous salt under modified conditions, and, on the other hand, the statement of Carius that prolonged contact of nitric oxide with ferrous sulphate induces further reduction of the nitric oxide. Thus, Abel and Bloxam found that when the nitrate was introduced into a boiling solution of ferrous sulphate containing an excess of sulphuric acid, nitrous acid was evolved, and some nitric acid remained unaltered even after prolonged boiling; and Eder¶ after demonstrating (at least inferentially from analytical results) that practically complete decomposition to nitric oxide results when the nitrate is put into a strongly acid and cold solution of ferrous sulphate in excess, and the heating made gradual, showed that under conditions otherwise similar excepting that the mixture was boil-

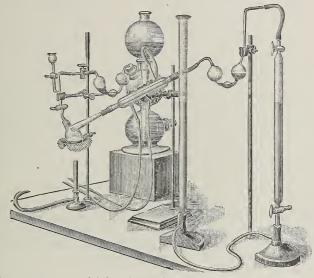
\* Zeitschr. für Anal. Chem., xxxi, 285. <sup>‡</sup> Journ. Chem. Soc., xxxii, 35. Journ. Chem. Soc., ix, 97.

+ Journ. Chem. Soc, xxxvii, 476.

§ Ann. Chem. u. Pharm., xciv, 138. ¶ Zeitschr. für Anal. Chem., xvi, 267.

ing when the nitrate was introduced, a higher oxide of nitrogen was evolved in quantity sufficient to be visibly red, while the oxidation of the ferrous salt in the residue fell to ninety per cent of its normal value.

These facts and the consideration that the analytical methods in which the nitric oxide is estimated give without exception unexpectedly low results have led me to look a little more carefully into the conditions under which the reaction of ferrous salts upon the nitrate may be expected to give the volume of nitric oxide most nearly approaching the theoretical yield.



The apparatus which I have found most satisfactory for this work consists of a small tubulated retort, upon the neck of which is fitted a small condenser to prevent loss of liquid during the distillation. Into the tubulature of this retort is fitted tightly, by a carefully ground joint, a tube drawn out so as to dip below the surface of the liquid, and fitted with carefully ground stop-cocks,—as shown in the figure,—and so branched above as to make it possible to transmit carbon dioxide through the apparatus, or to admit any liquid without admixture of air. The condenser is joined to a Will and Varrentrapp bulb used as a trap, and this in turn is connected by thick vacuum tubing with a Hempel gas-burette. Carbon dioxide was generated in a Kipp's apparatus by action of boiled hydrochloric acid upon boiled marble, and the liquid was charged with cuprous chloride, following Warrington's device, to take up traces of dissolved oxygen. Notwithstanding all precautions, I have met with the generally recognized experience in finding that the gas from the generator is never so pure that a hundred cubic centimeters of it will not leave a tiny bubble when shaken with a solution of caustic soda.

With the apparatus described the following experiments were made. Potassium nitrate (0.1 grm.) was introduced into the retort, generally in the dry condition, carbon dioxide was passed through the apparatus until the gas collected over sodium hydroxide left only the minute bubble which the gas from the generator alone had been found to give, and 40 cubic centimeters of a boiled solution of ferrous chloride in hydrochloric acid was admitted through the funnel tube, after shutting off the carbon dioxide and lowering the leveling tube of the Hempel burette. With the stop cocks arranged as in sketch, the liquid was then slowly heated to boiling and the process continued until the reaction of the ferrous salt upon the nitrate was apparently complete, when the carbon dioxide was again passed through the apparatus to secure complete removal of the nitric oxide, the absorption of the carbon dioxide being hastened by inclining and shaking the burette at intervals. The volume of the gas under existing barometric and thermometric conditions was noted. To discover how much of the gas collected was actually nitric oxide, I have found it best to absorb this gas by potassium permanganate. This is very easily and quickly accomplished by attaching a funnel to the Hempel burette through which a strong solution of potassium permanganate can be introduced. I have generally taken the precaution of adding water first in order to prevent the possibility of any local action between the potassium permanganate and caustic soda by means of which oxygen might be produced.

The following tables give the results of experiments performed in this way. In the first column is given the absolute volume of the gas unabsorbed by  $\text{KMnO}_4$ , in the second the per cent  $\text{KNO}_3$  reckoned as if the total volume were nitric oxide, and in the third the percentage reckoned from the absorbed nitric oxide. In cases where potassium iodide was used in the Will and Varrentrapp tube to break up any higher oxides of nitrogen that might be formed, the amount of iodine thus set free is given.

In experiment (3) of Table I, the ferrous chloride was made by dissolving iron wire in boiled hydrochloric acid, and the potassium nitrate was dissolved in boiled water and added to the ferrous chloride. With this dilution, the reaction proceeded very slowly and it was found necessary to add several successive portions of hydrochloric acid before the reaction was complete, but the results as finally obtained are quite comparable with those obtained by a more rapid process.

		1.					
	With potassium iodide in the Will and Varrentrapp tube.						
	Vol. of						
	unabsorbed gas.	total vol.	absorbed vol.	Iodine.			
(1)	$^{\cdot45}~\mathrm{cm}^{s}$	99.98	98.1	.0004			
(2)	·65	99.83	96.74	.0008			
(3)	·45	100.3	97.6	.0004			
(4)	·6	99.7	97.7	.0022			
		II.					
	With wat	er in Will and Va	arrentrapp tube.				
(1)	•6	97.76	95·				
(2)	•6	97.76	$95 \cdot 2$				
(3)	•6	97.9	95.2				
(4)	•6	97.4	94.7				
(5)	2.43	97.3	87.				

It will be seen by a glance at the tables that the best analytical results are obtained by the use of potassium iodide in the Will and Varrentrapp tube and calculation from the total volume of gas. The average of the results obtained above, omitting for a reason which will appear later the last experiment of the second series, may be expressed in this way :

Per cent from total gas	With KI. 99.95	With water. 97.7 95.0	Difference. 2.25
" " nitric oxide	97.53	95.0	2.53

Diff. 2.42

2.7

In each case there is an amount of gas equal to about 2.5per cent of the total volume which is not nitric oxide. In whichever way reckoned the total amount of gas collected is about 2.5 per cent greater when potassium iodide is used than when water is used in the Will and Varrentrapp tube. This would indicate that some higher oxide of nitrogen is formed and is decomposed by the potassium iodide with a liberation of nitric oxide equal to about 2.5 per cent of the total volume of gas. In case the formation of this oxide were due to traces of air which oxidized the nitric oxide to nitrous acid, the volume of nitrogen thus left would be, as has been shown, exactly equal to that of the nitric oxide oxidized, and therefore there should be about 2.5 per cent of gas incapable of absorption by potassium permanganate, which is practically found to be the case. This would furnish, then, a simple explanation of the results given. Supposing this explanation to be the correct one, the presence of air should not influence the total volume of gas in case potassium iodide is not used. To test this point, the last experiment of the second series was performed. This experiment was done in exactly the same way as the others except that the carbon dioxide was not allowed to pass through long enough to displace the air completely. It will be observed that the total volume of gas is practically the same as in the other experiments, but, as would naturally be expected, the volume of gas incapable of absorption by potassium permanganate is much increased.

An interesting confirmation of the supposition that small quantities of air introduced into nitric oxide confined over caustic soda would not influence the total volume of gas was found in some experiments performed later. After the nitric oxide in the Hempel burette had been accurately measured, air was introduced through the upper stop cock, a cubic centimeter at a time, and the burette lightly shaken. It was found that more than twenty cubic centimeters of air could be introduced in this way without materially affecting the total volume of gas, but that the volume began to increase when about one cubic centimeter of nitric oxide was left unoxidized, as subsequently determined by potassium permanganate.

In the fifth experiment of Table II, supposing the 2.43 cubic centimeters of unabsorbed gas to represent nitrogen left from air which had oxidized the nitric oxide to nitrous acid 2.5 cubic centimeters of nitric oxide would thus have been made to disappear, and the amount of nitric oxide left should be 89 per cent, 2 per cent higher than that obtained. On the same supposition, in the four preceding experiments, the .6 cubic centimeters of unabsorbed gas represent a loss of .6 cubic centimeters of nitric oxide which corresponds to a loss of about 3 per cent on the nitrate, so that the results reckoned from the absorbed gas should be about 97 per cent instead of 95 per cent as found. Here, again, is an unexplained loss of about 2 per cent. Moreover, with the use of potassium iodide, it is plain that, in whatever way these higher oxides of nitrogen may be formed, they should be entirely broken up into nitric oxide, so that the amount reckoned from the absorbed gas should be 100 per cent, whatever the total volume may be. We find instead that we get an average of 97.6 per cent, a loss of a little more than two per cent. It seemed probable, then, that as these experiments were done, there was a loss of from 2 to 2.5 per cent of nitric oxide by solution in caustic soda. This loss would mean the solution of 5 to 6 cubic centimeters of the gas after being thoroughly shaken with about 75 cubic centimeters of strong caustic soda, an amount of solubility which did not seem at all improbable and which would be quite in accordance with the results of Warington's experiments, previously mentioned.

The following set of experiments was therefore undertaken with the double object of studying the solubility of nitric oxide in caustic soda, and noting any conditions of temperature or proportions which might influence the course of the reaction. The same apparatus was used as in the preceding experiments except that a Geissler tube filled with water was inserted between the Will and Varrentrapp tube and the Hempel burette to prevent the possibility of any iodine being carried over mechanically into the gas receiver. In all cases the Will and Varrentrapp tube was filled with potassium iodide, and the amount of iodine liberated estimated by titration with sodium thiosulphate.

	III.	
	Per cent reckoned	Amount of
	from total vol. of gas.	iodine in grams.
(1)	99.	.0024
(2)	100.5	.0043
(3)	99.2	.0120
(4)	99.4	.0020
(5)	100.8	.00355
(6)	98.9	.0008

In the last five experiments of this series, the caustic soda solution was thoroughly boiled to eliminate any error which might arise from oxidation of the nitric oxide by air dissolved in the liquid, but with no marked difference in the results.

In all except the last one of these experiments, the nitrate and ferrous chloride were brought together in a more or less hot solution instead of being heated gradually, and although the amounts of iodine vary, it will be seen that they are on the whole greater in this series than in the experiments in which the reacting bodies were brought together in the cold. This would indicate the possibility of some slight local action in the hot solution by which higher oxides of nitrogen are generated, but any analytical error from this source is corrected by the use of the potassium iodide which converts them into nitric oxide.

In experiment (3) of this series, where a very large amount of iodine is liberated, only one half as much ferrous chloride was used in proportion to the amount of nitrate as was taken in the other experiments, so that the amount of iron present must have been very near the theoretical limit. Here the amount of iodine would indicate the formation of a higher oxide of nitrogen, an error corrected however by the use of potassium iodide so that the percentage as calculated from the total volume of gas compares well with the results obtained in the other experiments. In experiment (6) also, a rather small excess of the FeCl<sub>2</sub> was taken (:255 grms. Fe being weighed out, whereas :163 is theoretically required), but in this case the liquids were almost cold when brought together, and the amount of iodine set free is very small.

In several cases experiments were made to test the solubility of the nitric oxide in caustic soda. In experiment (2) the gas was allowed to stand over the liquid, with frequent shaking, for about an hour when the volume had decreased from 24.8 to 22.6 cubic centimeters. In experiment (3), after the lapse of an hour with similar treatment, the volume of gas had decreased four cubic centimeters, and one cubic centimeter was lost by the gas simply standing over night over caustic soda.

To determine whether the nitric oxide went into solution as such or in the form of nitrite, the following experiments were performed. About 30 cubic centimeters of the liquid were drawn off by stopcock at bottom of Hempel's burette into an acidified solution of potassium iodide, freely exposed to air, and the amount of iodine set free determined by fitration with sodium thiosulphate. Again, 30 cubic centimeters more of the same solution were treated in exactly the same way except that the flask containing the potassium iodide was first filled up with carbon dioxide and air carefully excluded. On two trials it was found that the amount of iodine set free under the latter circumstances was very small, and less than one-half as much as that set free when air was admitted freely, showing very plainly that some, and perhaps most, of the nitric oxide was dissolved as such, without chemical action of the caustic soda.

The principal conclusions to which this study of the estimation of nitrates, by measurement of the volume of nitric oxide swept along by carbon dioxide and collected over caustic soda, has led me, are as follows :

1. The best analytical results are obtained according to this method by passing the gas through potassium iodide before collection, and estimating from the total volume of gas collected.\*

2. If air be present in the apparatus at the outset, it will not affect the total volume of gas if potassium iodide be not used, or if the nitric oxide meet the air beyond the Will and Varrentrapp bulb. When potassium iodide is used, air in the apparatus would make the total volume too large, but with small amounts of air, this error is counterbalanced by the solubility of nitric oxide in caustic soda.

3. Since the nitric oxide is perceptibly soluble in caustic soda upon shaking, the gas should not be left long in contact with the liquid before the volume is measured.

4. If the hydrochloric acid used is very dilute, the reaction proceeds very slowly, but leads finally to the same results.

5. If the nitrate and ferrous salts are brought together hot, some higher oxides of nitrogen may be formed, but the error is corrected by the use of potassium iodide.
6. If potassium iodide is used the results are accurate even

6. If potassium iodide is used the results are accurate even when the ferrous chloride is present only in very slight excess.

<sup>\*</sup> This result accords with Glaser's experience in collecting the gases evolved unmixed with CO<sub>2</sub>, over KI—[loc. cit.]

## ART. XIX.—Concerning the Structure of Caoutchouc; by HERMANN F. LUEDERS.\*

WHILE examining a number of specimens of crude rubber from various regions, with regard to their impurities, my attention was directed to the microscopic characters of the rubber itself. The literature on the subject being scanty, it appeared as if a brief examination of the matter might be profitable. The following is a short summary of my results.

Being unable to procure fresh stems of any rubber-producing plant, except *Ficus elastica*, the succeeding details concerning the appearance and properties of the latex are taken from that plant only.

In Ficus elastica the caoutchoue is found in the copious latex which is contained in relatively narrow, branching vessels, abundant in the hypodermal and pith parenchyma. The caoutchoue exists in the form of small, colorless globules on the average  $3\mu$  in diameter; collected under oil of almonds it retains the original appearance for some time; in about half an hour the globules begin to coalesce, while at the same time, solid particles separate out of the menstruum in which the droplets are suspended. If the latex exudes in the air, the coalescence of the globules is very rapid and, with the evaporation of the watery material, results in the speedy formation of a transparent film, soluble in chloroform, ether, benzole, carbon disulphide and similar solvents.

There remains, however, an abundant white residue when the dried latex is treated with any of the above solvents. This residue consists of acicular or tabular crystals and grains. Its behavior in presence of acids and other reagents, before and after ignition, seems to indicate its identity with calcium oxalate, while traces of starch are also found to be present.

Faraday<sup>+</sup> found that a specimen of latex, brought in a sealed bottle from South America, had an acid odor. It does not appear from what plant the latex in question was derived, nor whether its acidity was original or due to fermentation. In *Ficus* the latex shows a weak alkaline reaction brought out only by delicate indicators. The coalescence of the caoutchouc globules under the influence of the air takes place quite rapidly and completely so that the solidified latex rarely shows any globules, nor have any of the specimens of crude rubber in the Harvard Botanical Museum, which I had the privilege

\* Presented to the American Academy of Arts and Sciences, Boston, by Professor Goodale.

+ Quar. Jour. of Science, Literature and the Arts, xi, p. 15, quoted by Wiesner.

of examining, shown the presence of rubber globules still distinct in the mass, although Wiesner\* states that he distinguished them in one variety.

But even if solidification obliterates all traces of the original globules, does not the rubber in its solid state show a structural arrangement common to all its varieties?

Payent claims for it an irregular reticulated structure, Wiesnert finds also many cases of reticulation, though also some where only a crumpled foliar structure was visible. Faraday on the other hand regards rubber as structureless. Of the twenty specimens which I examined no two agreed in their microscopic structure; three main types might, however, be distinguished. Namely (1) the blistery flowage (2), the reticulated, and (3) the stratified. Reticulation proves of infrequent occurrence, while stratification predominates. The coarse stratification can generally be shown to be parallel to the surface of the rubber mass, while solidifying. Most stratified specimens showed a system of crumpled, branching, or broken crosslines, such as might be formed by the shrinking of any drying layer. In some of the stratified specimens, peculiar illusory appearances are discernible resembling roughly the structure of wood-cells of certain conifers or in a few cases ducts of angiosperms. These misleading appearances are produced by particles of included dust, fragments of wood bark, and the like.

Different parts of the same sample are frequently found to possess unlike structure. These facts lead us to doubt not only the presence of a definite structure common to all kinds of rubber, but also of any structure distinctively peculiar to each one.

In order to place the above statement on a yet firmer basis I made chloroform solutions of various varieties of rubber. These were allowed to solidify and then sectioned and examined. Various markings were found, but none similar to those of the respective varieties before dissolving.

Caoutchouc then has no definite structure, *per se*, and all apparent structure is only the result of the conditions under which its coagulation from the latex, and subsequent solidification take place.

In Wiesner's discussion of the microscopic properties of rubber, occur the following statements: "all varieties of rubber so far as examined by me, appeared, between the Nicols of the polarizing microscope, in brilliant colors." "The polarization colors appear most striking if a thin section of caoutchouc is strongly compressed between two slides."\*

\* Wiesner. Rohstoffe des Pflanzenreiches, p. 158.
 ‡ Compt. Rendus, xxxiv.
 ‡ Rohstoffe, p. 164.
 § Rohstoffe, pp. 164, 165.

The latter statement suggested the question, whether the colors so observed, might not be merely the result of tension which must here undoubtedly exist in consequence of the pressure.

All samples on hand were examined with reference to this property. Thin sections were made with a razor, and placed without a coverglass on the stage of a polarizing microscope; every one of them displayed colors more or less striking.

Then arose the next question: the tension of pressure had indeed been obviated in the last series of tests, but might not the mechanical operation of cutting produce a tension on the surface of the adhesive rubber?

To answer this, several tests seemed applicable. By washing a section in chloroform, the superficial layer that might have been stretched in cutting could be removed. By cutting a section with a hot platinum wire, tension was not likely to be produced. By dissolving and then drying rubber it could be examined before any outside force, other than surface tension, could have influenced it. By examining fresh latex, liquid or dried, the properties of the original globules could be ascertained. The results of these different tests agree completely; no colors appear. When, however, the resolidified rubber or dried latex was sectioned however carefully or quickly, or stretched, colors invariably appeared. These results, and absence of polarization-colors whenever tension was removed, presence of colors where tension might exist, allow but one conclusion. The property of displaying various prismatic colors under the rotating Nicol of the polarizing microscope, probably does not belong as such to any of the varieties of crude rubber brought into our markets, and these colors so frequently noted are best explained as incidental results of the way in which the objects are generally prepared for examination.

ART. XX.—Fisher's New Hypothesis; by GEO. F. BECKER.

In the June number of this Journal<sup>\*</sup> Mr. O. Fisher reaches the conclusion that on an earth of small viscosity, that is a fluid globe, the height of the oceanic tides would be diminished by only a moderate fraction of its height on a rigid earth. He infers that the existence of tides of short period does not indicate a high value for the rigidity of the earth; a conclusion of great interest to geologists, some of whom per-

\* Vol. xlv, p. 464. 1893.

haps will not care to undertake an examination of the reasoning employed in reaching it.

Mr. Fisher obtains this unlooked for result by discussion of a formula of Prof. G. H. Darwin giving the height of the oceanic tide relatively to the nucleus on the "canal theory" for a yielding earth, whether the yielding is elastic or not. For comparison Darwin also states the height of the relative tide on the equilibrium theory for the same value of the potential.\* The formulas involve the lag of the tide, which disappears when the case of a fluid earth or that of a rigid earth is considered.

Neglecting the lag, the formula for the "canal theory" may be written

$$a_n - r = \mathbf{R} \left( 1 - 2\mathbf{A} \cdot \frac{2g}{5\tau} \right)$$

where r is the radius of the tidal water-surface,  $a_n$  the radius of the nucleus, R one-half the total amplitude of the tide on a rigid earth, g the acceleration of gravity, A (which Darwin denotes by E) the greatest semi-amplitude of the bodily tide at the equator and  $\tau$  is three times the moon's mass into the square of the earth's mean equatorial radius divided by twice the cube of the moon's distance.

The formula for the equilibrium theory under the same conditions is

$$r' - a'_n = \mathbf{R}' \left( 1 - 2\mathbf{A} \cdot \frac{2g}{5\tau} \right)$$

where the primed letters denote quantities corresponding to the same letters unprimed in the other formula.

From a comparison of the full formulas, equally applicable to those given above, Darwin points out that where the one formula gives high water the other gives low water. This is also the main difference between the theories.<sup>+</sup> Either formula gives the tide on a rigid nucleus when A is zero. For a'fluid homogeneous globe A is the same on either theory.

Mr. Fisher draws his own conclusions from an evaluation of  $2A \cdot 2g/5\tau$ , which he computes at 2/5 nearly. He infers that on the canal theory the tides cannot be less than 3/5 of their height on a solid globe.<sup>‡</sup> He might also by the same

\* Phil. Trans., vol. clxx. p. 26, 1879.

+ Compare Darwin's article on tides, Enc. Brit., 9th edition, vol. xxiii, p. 354, "tides inverted." The dynamical theory for an earth completely covered by the ocean would give tides of the same height as the equilibrium theory, if the ocean were 3.000 fathoms deep at the equator and shoaled towards the poles. In general its height depends on the distribution of depth. Ibid. section 15.

<sup>‡</sup> Proc. Cambridge Phil. Soc., vol. vii, 1892, p. 337.

process have concluded that the tides would show a corresponding amplitude on the equilibrium theory, as appears from the formulas stated above.

Mr. Fisher's computation is incorrect because he takes for A the value which it would have for a fluid globe, homogeneous or not, were there no mutual attraction between the fluid particles. It was for the purpose of dealing with the effect of this mutual attraction that the method of "spherical harmonics" was evolved. The effect in the case of a fluid globe of uniform density throughout on the equilibrium theory, is well known to be an increase in the ellipticity in the ratio 1 to 1-3/5. The ellipticity, e, of the equilibrium lunar tide, in a fluid earth, with this distribution of density, composed of mutually attracting particles is

$$e = \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{a^{3}\mathrm{M}}{\mathrm{D}^{3}\mathrm{E}},$$

where (as in Thomson and Tait, Nat. Phil.)  $\alpha$  is the earth's mean equatorial radius, D the moon's distance, E the earth's mass, and M the moon's mass.\*

Since the ellipticity is small, it is easy to see that 2A = aeand therefore also, since for this case  $E/a^2 = g$ , substitution for A and  $\tau$  of the values assigned to them above gives

$$2A \cdot \frac{2g}{5\tau} = \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{a^4M}{D^3E} \cdot \frac{2}{5} \cdot \frac{E}{a^2} \cdot \frac{2}{3} \cdot \frac{D^3}{Ma^2};$$

and here the second member reduces to unity by cancellation. In general, therefore, or irrespective of the fluidity of the earth, the quantity  $2A \cdot 2g/5\tau$  is simply the ratio of the greatest bodily equatorial tide in any special case to the equilibrium tide on a fluid earth. Thus for a fluid earth the canal theory and the equilibrium theory give the same result, viz: no relative tide, or

$$1 - 2A \cdot 2g/5\tau = 0.$$

On any theory yet propounded for the tides, the existence of semi-diurnal tides indicates an earth presenting great resistance to deformation. This resistance, so far as the tides are concerned, may be due either to rigidity or to the viscosity of an ultraviscous fluid, some 20,000 times as viscous as hard brittle pitch at 34° F. In the same paper by Darwin quoted above, he comes to the conclusion "that no very considerable portion of the interior of the earth can even distantly approach the fluid state."

Washington, D. C., June, 1893.

\* Compare Nat. Phil., section 819.

# ART. XXI.—Criticism of Mr. Fisher's Remarks on Rock Fusion; by CARL BARUS.

ALTHOUGH the experiments of Profs. Roberts-Austen and Rücker\* were made in answer to a query of Mr. Fisher's, I think he is laboring under a misapprehension as to their work. These gentlemen nowhere state that the rock was fused below 920°. What they do state is, "There is a large absorption of heat in the neighborhood of 800°, which raises the mean specific heat between 750° and 880° C., to the large value 0.636;" and in an earlier paragraph, "frequent heatings and coolings, and the nature of the flame—whether oxydizing or reducing—employed to heat the mass appeared to affect the results very seriously."

As the paper of Roberts-Austen and Rücker appeared about the time when I was making the diabase experiments, I looked forward to these anomalies (as I believed them to be) with interest—more particularly as Mr. King and I were on the lookout for polymerizations accompanied as they usually are with marked volume changes. But my results showed such commonplace smoothness throughout the stated interval of temperature that I gave up the chase. If, however, these anomalies are now to be interpreted as fusion, it is well to bear in mind that the melting point of silver is at about  $954^{\circ}$ ; and that if dolerite melts even below  $920^{\circ}$  (750° to 880° as given above) it ought actually to run on a surface of boiling zinc.

We did not try dolerite. True we had a list of rocks to put through the mill after it had been invented ;—but Congress in its wisdom saw no public value in our lucubrations and our efforts (with much else on our program) were foredoomed. It is with mingled feelings that one apologizes for one's toddling paces when there was good will enough for a journey!

However, to believe that dolerite can be slagged in a zinc pot or even fused in a candle flame is an exertion, and one is at liberty to ask the privilege of trying it.

Suppose for the sake of argument, that an absolute temperature  $920^\circ+273^\circ$  is inserted into Clausen's equation instead of  $1170^\circ+273^\circ$ . The effect would be to change the accepted relation of the increments melting point and pressure from

<sup>\*</sup> Roberts-Austen and Rücker, Phil. Mag., xxxii, p. 353, 1891. With regard to these experiments I have already expressed myself in Phil. Mag, xxxv, pp. 296, 305, 1893. The authors themselves state "As we have not definitely proved what is the cause of these discrepancies" (those of the above text being meant), "we publish our conclusions with a certain amount of reserve."

0.025 to 0.021; but this would not materially alter the diagrams, remembering that the other constants of the equations are found independently.

As to the latent heat of fusion, it is a question whether there is such a datum strictly speaking. What I did was to idealize the case, by slightly prolonging the rate at which liquid thermal capacity changes with temperature in the direction of lower temperatures and the rate at which solid thermal capacity changes with temperature in the direction of higher temperature. The admissibility of such a process is a question of experiment; and experiment sustains it because the two loci very nearly overlap. Thus one can state that if diabase fused at such a temperature its latent heat would be so and so. The temperature to be taken is clearly the melting point obtained in the volume work.

Now, as Mr. Fisher will acknowledge, mere statements of melting point and latent heat for dolerite are inadequate, so long as the volume changes at fusion are missing. He might have made a much more startling statement by comparing diabase and naphthalene, for instance; the latter has a latent heat say twice as great as the former, in spite of the fact that diabase melts at a temperature enormously high as compared with the other body. In all this there is nothing implied either with reference to the law of fusion in question or the isometrics.

In the case of diabase, granting merely that the volume changes experimentally observed are correct, the following mean values\* hold good :

> Melting point 1200° C.,  $dT/dp \doteq 020$ " " 1100 C., dT/dp = 027" " 1000 C., dT/dp = 027

To go below this it would be necessary to actually work out the relation of thermal capacity to temperature for liquid diabase. Nevertheless the data given are sufficient to show, that the lower melting point for which Mr. Fisher is angling would only accentuate our cardinal result, viz: that the rate at which melting point increases with pressure is about the same in silicates and in organic compounds. My conviction of the essential correctness of Mr. King's constructions is therefore unshaken.

\* T being the absolute melting point at the pressure p in atmosphere.

# ART. XXII.—Larval forms of Trilobites from the Lower Helderberg group; by C. E. BEECHER. (With Plate II.)

ATTENTION has previously been called to the abundance and perfection of fossils in the siliceous limestones of the Lower Helderberg group, from a limited locality in the Helderberg Mountains, south of Albany, New York. Proper methods of collecting and preparation yield quantities of the most delicate and exquisitely preserved animal remains, consisting chiefly of bryozoa, with numerous brachiopods, ostracodes, spicules of sponges, small corals, lamellibranchs, gastropods, and disarticulated trilobites. Remains of hydrozoa, echinodermata, annelids, pteropods, and cephalopods, are less frequent.

The conditions of preservation are such that not only are the large and strong species preserved, but also the smallest, and the young of many in all stages of growth. As would naturally be inferred, the study of this fauna, based upon such complete material, has brought to light many undescribed species, and has increased the range of known genera, besides affording several genera new to science. Altogether about seventy new species are now known to the writer.

Among the rarities discovered are the specimens here noticed, consisting of five larval trilobites referred to the genera *Acidaspis* and *Phaëthonides*. They represent early stages of these genera when the animals had no thoracic segments, and when the separation between the cephalon and pygidium was not distinctly marked.

Notwithstanding the abundance of trilobites in the Paleozoic rocks, and the care with which they have been studied and collected, but few are known in the early adolescent state, and extremely few in the still earlier larval stages. This paucity of larval specimens seems to be due chiefly to the sediments, which, in general, have not been favorable for the preservation of such organisms. Heretofore, the best material has come from fine shales and slates representing original muds. The most complete developmental series known are the classic ones of Barrande,\* representing Aeglina, Agnostus, Arethusina, Arionellus, Dalmanites, Hydrocephalus, Sao, and Trinucleus, of which Agnostus, Dalmanites, Hydrocephalus (= Paradoxides), Sao, and Trinucleus, were observed in their larval stages.<sup>†</sup>

\* Systême Silurien de la Bohême, i, 1852.

† Hydrocephalus appears to be the young of Paradoxides. See Barrande, l. c., and compare Hydrocephalus carens, Pl. 49, H. saturnoides, Pl. 49, with Paradoxides inflatus, Pl. 13, figs. 16, 17, 18, and P. spinosus, Pl. 12, figs. 5, 6, 7 The first American larval trilobites were discovered and described by S. W. Ford.\* They were specimens of *Elliptocephala* (*Olenellus*) asaphoides Emmons, from near Troy, N. Y., and together with the larvæ of *Sao hirsuta* were the most elementary forms known.

Next, C. D. Walcott, in 1879,<sup>†</sup> published a fine series illustrating the metamorphoses of *Triarthrus Becki* Green, from the Utica Slate. All the stages were shown, from an individual with one thoracic segment to mature specimens having thirteen to sixteen segments.

G. F. Matthew, in 1887 and 1889,<sup>‡</sup> carefully described and illustrated embryonic and immature forms of *Ptychoparia Linnarssoni* Brögger, *Liostracus ouangondianus* Hartt, and *Solenopleura Robbi* Hartt, from the slates at St. John, New Brunswick. The youngest forms were quite as primitive as the *Sao* of Barrande and *Elliptocephala* of Ford, so that the larvæ of at least five genera have been described, representing the same early stage.

The orders of development recognized by Barrande are:

I. {	Head predominating, incomplete. Thorax nothing or rudimentary. Pygidium nothing.	TYPES. Sao hirsuta.
(	Head distinct, incomplete. Thorax nothing. Pygidium distinct, incomplete.	Trinucleus ornatus and all Agnostus.
	Head complete.	Arethusina Konincki.
(	Head complete. Thorax complete. Pygidium distinct, incomplete.	Dalmanites Hausmann <b>i</b> .

The third and fourth orders are probably later stages of the first and second, and it now seems that the second order will be found to have an earlier stage equivalent in structure to the first.

The larvæ noticed in the present paper are of peculiar interest on account of their belonging to highly ornamented and specialized genera. Moreover, some deductions can now be made concerning the permanence and uniformity of the stages of metamorphoses, as well as the acceleration of specific characters so that they appear in the larval state.

\* This Journal, vol. xiii, p. 265, 1877.

† Transactions of the Albany Institute, vol. x.

‡ Illustrations of the Fauna of the St. John Group, No. IV, Trans. Roy. Soc. Canada, 1887. Sur le Développment des premiers Trilobites, An. Soc. Roy. Macol. Belgique, xxiii, 1889.

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## A larval form of Acidaspis.

Two species of the family Acidaspidæ are known from the rocks of the Lower Helderberg group in New York, *Acidaspis tuberculatus* Conrad, and *Dicranurus hamatus* of the same author. Both are so different that the larva figured on Plate II, figures 5, 6, 7, can be referred to the first without hesitation, since it retains one of the most characteristic features, viz: the denticulate cephalic border.

Three individuals of *Acidaspis tuberculatus* have been found in the same early stage of development. The length of the best specimen exclusive of the spines is  $93^{\text{mm}}$ ; width  $88^{\text{mm}}$ . The total length is  $1\cdot3^{\text{mm}}$ .

The general outline is longitudinally semi-ovate, regularly rounded in front, and truncate behind; greatest width across the anterior third. Lateral and anterior margins bearing about thirty-five alternating spines or denticulations. Each posterior lateral angle is produced into a strong spine, and between them on the margin are four smaller ones. Upper or dorsal surface convex, highest posterior to the mid-length, and abruptly bent down or truncate behind.

All but the posterior truncate portion is believed to be homologous with the cephalon of an adult form, so that the posterior angles are really the genal angles. The axis is defined, convex, narrow, widest in front, and apparently divided into six annulations or lobes. The posterior one doubtless represents the axis of the pygidium, since it is limited by a furrow extending to the bases of the genal spines. The next anterior lobe would then correspond to the occipital ring, and the others to the lobes of the glabella. Two lunate prominences on each side of the axis in front are the palpebral lobes and the eyes.

On the ventral side, Plate II, figure 6, the edge of the cephalon is extended inwards, making a continuous doublure. The axial depression extends the entire length of the animal, and is divided into lobes or annulations by transverse ridges, which represent muscular fulcra and points for the attachment of appendages.

## A larval form of Phaëthonides.

The larva figured on Plate II, figures 8, 9, 10, cannot at present be referred to a particular species. Only two species of *Phaëthonides* have yet been described from the Lower Helderberg, but from additional material it is now evident that other species occur in these rocks. Moreover, if this larva retains its specific characters as strongly as *Cyphaspis* tuberculatus, it cannot be referred to either *Phaëthonides*  cyclurus Hall, nor to P. macrobius Billings, sp., as it has a strongly denticulate posterior border, a character not possessed by either of the described species. The generic reference can be determined with more certainty, for the combination of features in the cephalic and pygidial regions cannot well exist in any genus except Phaëthonides found associated with this larva.

The outline is broadly elliptical transversely, and obtusely angular at the genal extremities. The cephalic portion is semielliptical, and includes more than half the animal. It has a narrow, flattened, entire border, and is defined posteriorly by the obtuse points, which are correlated with the genal angles. Palpebral lobes prominent, and, as in the larva of Acidaspis, situated nearer to the anterior margin than to the frontal lobe of the axis.

The pygidial portion is depressed convex, with five pairs of symmetrically disposed marginal denticulations or spines, of which the median pair is short.

Axis narrow, extending nearly the entire length of the animal, obscurely annulated by six or seven (possibly eight) slight constrictions. The anterior five seem to pertain to the cephalon and the others to the pygidium. The annulations each carry a single pair of spines, with the exception of one at the junction of the cephalon and pygidium, which apparently has but a single spine.

The pleural and lateral facial areas also bear double rows of spines, the anterior pairs being between the eyes and axis. The distinction between the cephalon and pygidium is very obscure, but the apparent large size of the latter in Phaëthonides may indicate a moult later than the first. The ventral side, figure 9, shows a narrow doublure and the axial cavity. Greatest length, 1.15<sup>mm</sup>; greatest width, 1.34<sup>mm</sup>.

## Observations.

Many correlations have been drawn between the Trilobita and other Arthropoda, by Packard, Dohrn, Lang, and others. The present state of opinion is well expressed by Lang,\* who concludes that the Trilobites are related to the Crustacea. In support of this is "the fact that the trunk feet are biramose and carry epipodial appendages." The important discovery by Mr. W. S. Valiant, of organs which can be homologized with antennæ, as announced by Mr. W. D. Matthew, + estab-

<sup>\*</sup> Text Book of Comparative Anatomy, English edition, p. 415, 1891. † On Antennæ and other Appendages of Triarthrus Beckii, by W. D. Matthew, read before the N. Y. Acad. of Sci., May, 1893. The first specimen preserving the antennæ was discovered by Mr. W. S. Valiant several years since. Recently Mr. Valiant and Mr. M. Sid. Mitchell have obtained other specimens showing more completely the nature of the appendages.

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lishes the comparisons made by Lang, so that the five cephalic limbs of Trilobites would correspond "to the 5 typical limbs of the Crustacean head, and the Trilobites might then be regarded as original *Entomostraca*, to be derived from the same racial form as the *Phyllopoda*" (Lang). Also, the phylogeny and relations of *Eurypterus*, *Limulus*, and the Trilobites, are with the Crustacean radicle. The information now at hand admits of still further conclusions regarding the affinities of the *Trilobita*.

The larvæ of Acidaspis and Phaëthonides, together with those of Sao, Elliptocephala, and Ptychoparia, indicate that Agnostus is neither the phylo-typembryo nor the phylo-phylembryo, but is really the adult equivalent to an early segmented stage of the higher genera. The characters of the youngest larvæ expressed in the non-differentiation of the cephalon and pygidium, the preponderance of the cephalon, carrying at this time all the appendages, some of which are the antennæ, are strong indications of the likeness of this stage to the Nauplius or Meta-nauplius of true Crustacea. No ocelli are known, however. The early segmented stages must have resembled, more or less, such late larval Crustacean forms as the larva of Bopryus, one of the Isopoda, and, as suggested by Woodward and Edwards, the Trilobita may be considered as ancient or proto-isopods.

The fact that most of the smallest larvæ observed belong to the first order of Barrande, and that the second and succeeding orders represent, more or less closely, stages of development of an individual from the first, is strong evidence that the first order, or the unsegmented condition, with dominant cephalon and undefined pygidium, is the primitive stage. It is therefore probable that, with more complete material, the young of *Trinucleus*, *Agnostus* (= types of 2d order), *Arethusina Konincki* (= 3d order), *Dalmanites Hausmanni*, *Proëtus*, etc. (= 4th order), will be found to have a first larval stage like *Sao*, *Ptychoparia*, and *Acidaspis*, thus bringing all into perfect accord.

Upon this basis, the following classification of the stages of development is suggested :

Nauplius ? {	Cephalon predominating, other parts not separated from it. Examples: earliest known stage of Sao, Ptychoparia, and Acidaspis.
	Cephalon distinct. Thorax nothing. Pygidium distinct. Examples : 2d stage of <i>Sao</i> , etc., and Bar- rande's larvæ of <i>Agnostus</i> and <i>Trinucleus</i> .

Nepic (As many stages normal thora segments.)

Nea

Ephe

	( Cephalon distinct.
	Thorax incomplete.
nic	Pygidium distinct.
ร ลร ์	Examples: Agnostus, Microdiscus, and
acic	young of all trilobites lacking full num-
	ber of thoracic segments.
	Cephalon distinct, complete.
	Thorax distinct, complete.
nic <	Thorax distinct, complete. Pygidium distinct, complete.
	Growth incomplete.
1	All parts complete, and full
bic	size attained

It is interesting to note that while neither the larvæ of Acidaspis nor Phaëthonides possess the characteristic generic features of sutures and glabellar lobation, yet their specific facies is quite pronounced. The larval Acidaspis does not suggest Acidaspis nor Ceratocephala in general; as Ceratocephala Verneuili Barr., Solenopeltis Buchi Barr., Dicranurus hamatus Con., or Ancyropyge Romingeri Hall, but has manifest likenesses to its own species, Acidaspis tuberculatus, and other closely allied forms, as A. Brighti Murchison, A. Hoernesi Barr. and also several species of Odontopleura, which in their adult form resemble the species of Acidaspis in every way except in the absence of the occipital spine.

Yale Museum, New Haven, Conn., June 10th, 1893.

### EXPLANATION OF PLATE II.

#### Acidaspis tuberculatus Con.

FIGURE 1.—Cephalon of an adult specimen.  $\times 2$ .

FIGURE 2.—Pygidium of a mature individual. × 2. FIGURE 3 — Pygidium of an immature individual. × 5.

FIGURE 4.—Segment of thorax; showing spines and ornamentation. × 2.

FIGURE 5.-Dorsal view of larva. × 38.

FIGURE 6.—The same; ventral view.  $\times 38$ .

FIGURE 7.—The same; profile, slightly oblique. × 38.

Lower Helderberg group, Albany Co, N. Y.

#### Phaëthonides, sp.

FIGURE 8.-Dorsal view of larva. × 38.

FIGURE 9.—The same; ventral view.  $\times$  38.

FIGURE 10.—The same : profile, slightly oblique. ×38.

Lower Helderberg group, Albany Co., N. Y.

## SCIENTIFIC INTELLIGENCE.

## I. PHYSICS.

1. Flame Spectra at High Temperatures. Part I. Oxyhydrogen Blowpipe Spectra, by W. N. HARTLEY. (Abstract, received from the author, of a paper presented to the Royal Society, May 10, 1893.)—Brewster, in 1842, first examined the spectra of salts with a flame of oxygen and coal-gas (Proc. Roy. Soc. Edinb., vol. vi, p. 145). Professor Norman Lockyer has given us maps of twenty-two metallic spectra at the temperature of the oxygen and coal-gas flame. The region observed lies between  $\lambda$  7000 and 4000.

Preparatory to undertaking the study of spectroscopic phenomena connected with the Bessemer "blow" and the manufacture of steel generally, I have carefully observed the spectra of metals and metallic oxides obtained by submitting the substances to the oxyhydrogen flame.

Method of Investigation.—The method of obtaining spectra with flames at high temperatures is the following: Hydrogen proceeding from a large lead generator is burnt in a blowpipe with compressed oxygen. The blowpipe measures 3 inches in length by  $\frac{3}{8}$  inch external diameter. The substances examined are supported in the flame on small plates of cyanite about 2 inches in length,  $\frac{1}{20}$  inch in thickness, and  $\frac{1}{4}$  inch in width. This mineral, which is found in masses in Co. Donegal, contains 96 per cent of aluminium silicate, and is practically infusible. The spectra were all photographed with the instrument employed by me on former occasions for photographing ultra-violet spectra, illustrations of which were published in the Chem. Soc. Journ., vol. xli, p. 91, 1882. The dispersion of the instrument was that of one quartz prism of 60°.

Isochromatic plates developed with hydroquinone were largely used. Various dyes for sensitizing and all kinds of developing substances were tried. The spectra were measured with an ivory scale divided into hundredths of an inch, and directly applied to the photographs, the division 20 on the scale being made to coincide with the yellow sodium line which appears in every photograph. It was found convenient to record the measurements on a gelatino-bromide paper print taken from an enlarged negative. Sometimes, for more careful and minute reference, it was found convenient to make an enlargement of the spectrum with the scale in position, but accurate measurement cannot be made in this way. It is necessary to use a low magnifying power and cross-wires in the eye-piece.

For the identification of lines already known nothing more complicated is required, but to measure new lines and bands it was considered desirable to make use of a micrometer and microscope; the screw of the micrometer was cut with 100 threads to the inch, and the magnifying power generally used was 10 diameters.

Characters and Extent of the Spectra observed.—Just as in the ordinary use of the spectroscope we must be prepared to see the lines of sodium, and in hydrocarbon flames the bands of carbon, so in these spectra the sodium lines and the strongest lines belonging to the emission spectrum of water vapor are also always present.

In addition, the cyanite yields the red line of lithium, which is no inconvenience, but a positive advantage, serving as it does, to indicate where the spectra commence.

A large majority of the metals and their compounds all terminate somewhere about the strongest series of water vapor lines. Typical non-metallic spectra are sulphur, selenium, and tellurium; the first yields a continuous spectrum with a series of beautiful fluted bands; the second a series of fine bands, occurring at closer intervals; the third is characterized by bands still closer together and near the more refrangible termination of which four lines occurring in Hartley and Adeney's spark spectrum of tellurium are visible. Increase in atomic mass causes shorter periods of recurrence of bands. In line spectra it is the reverse; increase in atomic mass causes greater periods in the recurrence of lines. Charcoal and carbon monoxide yield chiefly continuous spectra; the latter, however, exhibits some carbon lines. The hydrocarbons yield the well-known spectrum of carbon bands with also those attributed to cyanogen. Of metallic elements, nickel, chromium, and cobalt yield purely line spectra; antimony, bismuth, silver, tin, lead, and gold beautiful banded spectra (spectra of the first order) accompanied by some few lines. The spectra are finer than those of selenium and tellurium.

Iron and copper exhibit lines, and, less prominently, bands. Manganese has a beautiful series of bands and a group of three very closely adjacent lines. Aluminium gives a fine continuous spectrum with three lines, origin uncertain, zinc a continuous spectrum without lines, and cadmium a spectrum consisting of one single line only,  $\lambda$  3260 2.

Of compounds, chromic trioxide yields a continuous spectrum with six lines belonging to the metal, copper oxide a fine band spectrum with two lines of the metal, magnesium sulphate gives a spectrum of magnesium oxide consisting of broad degraded bands composed of closely adjacent fine lines and one line belonging to the metal,  $\lambda$  2852.

The sulphates of calcium, strontium, and barium give both bands of the oxides and lines of the elements. Phosphorus pentoxide yields a continuous spectrum with one peculiar line, seen also in the spectrum of arsenic.

The chlorides of the alkalies give also lines of the elements with a more or less continuous spectrum, which, it is believed, is due to the metal in each case. Lithium chloride gives no continuous spectrum. The Volatility of Metals.—One of the most interesting facts ascertained by this investigation is the volatility of all the metals examined, except platinum, and particularly the extraordinary volatility of manganese, and, to some extent, of the infusible metal iridium. Metal believed to be pure iridium is seen to have diminished after the flame has played upon it for about two hours.

2. New Calcium Lines.—J. M. EDER and E. VALENTA state that they have discovered a new group of calcium lines in the ultra violet. These lines appear by the use of strong induction sparks and have the following wave lengths (*i* denotes relative brightness, for the strongest calcium line i=10, and for the weakest i=1):

	i		i
$\lambda = 2276.0$	3	$\lambda = 2140.3$	3
2259.5	1	2133.0	1
2208.3	4	2131.2	1
2200.5	1	2123.0	1
2197.6	3	2112.9	3
2170.0	1	2103.2	2
2152.3	1		

- Wien. Anz., 1892, p. 252-253.

3. The Hall Effect in Iron, Cobalt and Nickel.—KUNDT has examined this effect in thin layers of the metals deposited by electrolysis on platinized glass, and states that in the three metals examined the Hall effect is proportional to the rotation of the plane of polarization of light in these metals in a magnetic field, and since the rotation of the plane of polarization in these metals is proportional to the magnetizing force, therefore the Hall effect is proportional to the magnetizing force. He states as a curious fact that electrolytically deposited bismuth shows a very weak Hall effect whereas cast bismuth shows the effect to a great degree.— Ann. der Physik und Chemie, no. 6, 1893, pp. 257-271. J. T.

J. T.

4. Measurement of Electrical Resistance by means of alternating Currents.—F. KOHLRAUSCH in an important paper discusses the limits of the method which owes its elaboration to him. Other observers have criticized the method and the author takes up their criticism and discusses the results which have been obtained. He states that fluid resistances as high as 100,000 ohms can be measured with precision by his method. He shows how the introduction of condensers can in certain cases increase the accuracy of the measurements. The want of symmetry of the telephone which is employed on the Wheatstone Bridge is also discussed.—Ann. der Physik und Chemie, no. 6, 1893, pp. 225– 256. J. T.

5. A New Form of Induction Balance.—The Hughes induction balance is an instrument of great sensitiveness, but it has not come into use in the measurement of specific resistance, for absolute measurements cannot be made with accuracy by means of it. It is true that Overbeck and Bergman have reached a fair degree of accuracy in the use of the balance, but the metals measured had

### Physics.

to be in the form of very thin plates. M. Wien shows how measurements can be made without resorting to a comparison with a standard metal—in other words, how absolute measurements can be made. In his method (1) one is independent of faults of contact and thermal effects at contact. (2) The measurement is made on metals in their natural state before they are influenced by wire drawing. (3) The specific resistance can be measured without determining a length.—Ann. der Physik und Chemie, no. 6, 1893, pp. 306-346. J. T.

6. Specific Resistance of Mercury.-J. V. JONES, adopting Lorenz's method of determining the ohm, has made a comparison of the ohm with the mercury unit and obtains the value

## 1 ohm = 106.307 mercury units.

## -Phil. Trans. Roy. Soc. London, 1891, vol. clxxxii, pp. 1-43.

#### J. T.

7. Photography of the Hertz Spark.—EMDEN has examined the sparks produced by electrical resonance by means of a revolving mirror and photography and finds that they are oscillating sparks. —Arch. d. Gen. III, xxvi, p. 483, 1891. J. T.

-Arch. d. Gen. III, xxvi, p. 483, 1891. J. T. 8. Green's use of "potential"; by GEORGE F. BECKER. (Com-municated.)-In the course of a paper\* crediting D. Bernoulli with the introduction of the word potential into physics and arguing that Gauss's noun, the potential, was suggested by Bernoulli's term, I made the statement "Green did not use the name potential but only the adjective." I find that this statement requires a qualification. In his paper of 1828 on electricity and magnetism, the word potential occurs at least 125 times, and of these it appears as an adjective qualifying function in 124 cases. Once, however, in section 5, Green uses the phrase "the value of the potential for any point," thus printed both in the Crelle reprint and in Green's collected works. At first sight this seems a substantive use of the word, but I think this interpretation would be erroneous. Had he intended in this passage to introduce a new synonym for potential function, and to invent a noun not heretofore employed in any language, some explanatory phrase would almost certainly have indicated as much, and the use of the new term would surely have been repeated. There is no such phrase; and I have read the whole memoir twice through for the purpose of detecting a second case of the substantive use of potential, without success. Those who read Green's paper before the year 1840 can only have supposed that the phrase in section 5 was intended to be "the value of the potential function for any point"; for to such readers potential was known only as an adjective. It seems nearly certain, therefore, that either Green or his printer omitted the word function in this one instance by mere accident. Had Gauss never introduced the noun, no one, it seems to me, would ever have asserted on the strength of this passage that Green used potential as the name of function.

\* This Journal, vol. xlv, p. 97, 1893.

9. The Physical Review: A Journal of Experimental and Theoretical Physics, conducted by EDWARD L. NICHOLS and ERNEST MERRIT. Vol. I, No. 1, pp. 1-80, July—August, 1893. (Published for Cornell University. Macmillan and Company, New York and London).—This new Journal gives the department of Physical Science what it has not had before in this country, a special periodical devoted to itself. The objects of the Physical Review, as given in the prospectus, are threefold: "To afford a channel for the publication of the results of research; to translate and reproduce in full, or in part, important foreign memoirs not easily accessible in the original to American readers; to discuss current topics of special interest to the student of Physics." It will be issued bi-monthly. The faithful carrying out of this program and the high standard of the Review in all parts is guaranteed by the able editorship of Professors Nichols and Merritt. It will doubtless receive from Physicist and the Scientific public in general the generous welcome which it deserves, and it should exert a powerful influence on the development of physical science in this country.

The opening number contains the following articles: The transmission spectra of certain substances in the infra-red by Ernest F. Nichols; relation between the lengths of the yard and the meter by W. A. Rogers; the infra-red spectra of the alkalies by Benjamin W. Snow (from Wiedemann's Annalen); the critical current density for copper deposition and the absolute velocity of migration of the copper ions by Samuel Sheldon and G. M. Downing; a geometrical proof of the three-ammeter method of measuring power by Frederick Bedell and Albert C. Crehore. The number closes with notes of scientific meetings and book notices. The mechanical execution of the work is all that could be desired.

10. Polarization Rotatoire. Réflexion et Réfraction vitreuses; Réflexion Métallique.—Leçons faites a la Sorbonne en 1891-1892, par G. FOUSSEREAU, rédigées par J. Lemoine. 343 pp. 8vo. Paris, 1893. (Georges Carré, Editeur).—This is an interesting and instructive volume discussing the whole subject of rotatory polarization. The method is simple and involves no excess of mathematical analysis. The four divisions under which the subject is treated, are: (1) natural rotatory polarization; (2) magnetic rotatory polarization; (3) vitreous reflection and refraction; (4) metallic reflection.

## II. GEOLOGY AND NATURAL HISTORY.

1. Lehrbuch der Petrographie von F. ZIRKEL. Vol. I. Leipzig, 1893. 8vo. 845 pp. (Verlag von W. Engelmann).—Prof. Zirkel was not only one of the earliest petrographers, but was particularly the first of the European workers in this line who became well known to the American scientific public through his connection with the work of the survey of the 40th Parallel under Mr. Clarence King. Therefore this work from his pen, in his chosen field after so long a silence—the reasons for which he states in the preface—will be without doubt eagerly welcomed and read by American petrographers and geologists.

The first volume, now issued, treats in the main of methods of petrographical research, the use of the microscope, of polarized light, of methods of separation and microchemical tests. Then follows the microscopical physiography of the more important rock-making minerals, which are treated in detail only in respect to those points which are of immediate petrographical interest. The list of minerals thus made out has been somewhat arbitrarily selected—thus we note that vesuvianite, although common in contact metamorphic areas, is omitted, while dumortierite, for example, is given. No cuts of any kind are introduced, the author stating his reason in the preface for omitting them.

This portion of the subject occupies about half the volume, the remainder is taken up with general petrography-the various types of structures (comprising really texture as well) of rocks are then given, their general methods of geological form, of alterations by weathering, by contact metamorphism and dynamic forces, etc. Then the igneous rocks are taken up, and treated from a general standpoint, their chemical relations, processes of crystallization, differentiation of magmas, etc, ending with their classification. It would be impossible here to review this part of the work as it deserves :-- suffice it to say that Prof. Zirkel divides the rocks for purposes of classification according to their mineral constitution, i. e., according to the feldspars or the lack of them, then according to structure which goes hand in hand with their geologic position, that is, plutonic or effusive. For the effusive (or porphyritic) rocks the distinction of geological age is retained, the rocks thus being divided into paleo- and neo-volcanic. Rosenbusch's family of the "dike rocks" is not recognized.

While it is probable that many petrographers will not agree with Prof. Zirkel on various points of theory and classification all will be thankful to him for the patient industry and rare discrimination with which he has brought together and digested such a vast amount of facts and material. These volumes when completed will form a work which no active investigator in this field can afford to do without. It is to be hoped the work will eventually be thoroughly indexed. L. V. P.

2. Ueber dus Norian oder Ober-Laurentian von Canada, by F. D. ADAMS.—Of this memoir, in which Dr. Adams sums up the results of five years' work in the field supplemented by further study with the microscope and in the laboratory, it may be justly said that it is one of the most important contributions to the proper understanding of the Archæan in Canada that has yet been made. It is impossible to give here even a brief summary of the results attained. He proves that the so-called "anorthosite" rocks of Canada are of igneous character, that they have broken through the Laurentian and are in general massive in structure. In the neighborhood of the gneisses the rocks exhibit a peculiar cataclastic structure and are here only, gneissoid. They are shown to have an enormous geographical extension—in the Saguenay region the anorthosite extends over 5,000 square miles. It is concluded that these rocks were intruded around the shore lines of the ancient Archæan continent in pre-Cambrian times as modern volcanoes fringe the great oceanic areas.—N. Jahrb. Min., B. B., viii, pp. 419–498. L. V. P.

3. Brief notices of some recently described Minerals.—SUNDTITE is a sulph-antimonate of silver and iron described by W. C. BRÖGGER from the silver mines of Oruro, Bolivia. It occurs in complex orthorhombic crystals and in massive forms. It shows no distinct cleavage, is very brittle and has a conchoidal fracture. Other characters are : hardness 3.4; specific gravity 5.50; luster metallic; color steel-gray. An analysis by G. Thesen gave

S	Sb	Ag	Cu	Fe
35.89	45.03	11.81	1.49	6.28=100.80

This leads to the formula (Ag<sub>2</sub>, Fe)S. Sb<sub>2</sub>S<sub>3</sub>. The species is named after the mining director, L. Sundt.—Zeitschr. Kryst., xxi, 193, 1893.

MARSHITE is native copper iodide described by C. W. Marsh from Broken Hill, New South Wales, and named after the describer by Prof. LIVERSIDGE. It occurs in very minute crystals implanted on a gossan-like siliceous cerussite. The crystals are referred to the hemihedral division of the tetragonal system. They are brittle; fracture subconchoidal; luster resinous; color reddish oil-brown; streak orange-yellow; transparent. The qualitative blowpipe and chemical characters fix the composition as iodide of copper, but a fuller examination of this and associated minerals is promised.—*Proc. Roy. Soc. N. S. W.*, xxvi, 326, 1892.

BURMITE is a new fossil resin from Upper Burma, described by Dr. Fritz Noetling in the Records of the Geological Survey of India, vol. xxvi, Part 1, 1893.

4. Zoisite from the Flut Rock mine, Mitchell Co., North Carolina; by W. E. HIDDEN. (Communicated.)—A pink, vitreous mineral, which I found entirely surrounding a large ovoid mass of very pure monazite, associated with a black, glassy allanite, has proved to be zoisite. The rare association made an analysis seem desirable, and this has been obtained through the kindness of Mr. L. G. Eakins of the U. S. Geological Survey. Mr. Eakins's analysis gave:

SiO2	$Al_2O_3$	$\mathrm{Fe}_{2}\mathrm{O}_{3}$	MnO	CaO	$H_2O$
38.98	31.02	4.12	0.23	23.80	2.03 = 100.21

Sp. gravity 3.352 at 27° C. The water is strongly combined, not beginning to go off until a red heat is reached.

5. Optical examination of Cacoxenite; by LEA McI. LUQUER. (Communicated).—The examination was made with a Beck lithological microscope, upon specimens from the following localities: Trenic, Bohemia; Zbiroff, Bohemia; Weilburg, Baden; Zwickau, Saxony; Bearville, Lancaster Co., Penn., and Lobenstein, Russia. In general the crystals were exceedingly minute, and very much extended in the direction of one axis. The largest crystals noticed were from Lobenstein, but even these did not exceed 0.04<sup>mm</sup> in thickness. They all showed extinction parallel and at right angles to the long axis, and the larger crystals polarized in rather bright colors. The pleochroism was very slight, only being observed in the case of one or two of the largest crystals, when the color was an orange-yellow in the direction of the long axis and a light yellow at right angles to this axis. The average crystals from Zbiroff, were slightly larger than those from the other localities. In general the crystals appeared to be terminated by cleavage or pinacoidal planes at right angles to the long axis, although in some cases pencil-pointed terminations were noticed and also oblique and irregular terminations and fractures.

Two of the largest crystals from Lobenstein, showing terminations, were examined with the following results. In one case the terminations resembled pyramid or dome faces with the apex truncated by a pinacoid. Angle between pyramid or dome faces over the vertex =  $74^{\circ}$  20'; angle (supplement) between these faces and the long sides of the crystal  $= 37^{\circ} 10'$ . Angle between pinacoid and sides of crystal = 90°. In another case the terminations resembled pyramid or dome faces without any pinacoidal truncating plane. Angle between these faces over vertex  $= 90^{\circ}$  (approximately). These measured angles would give an axial ratio of 1:3. Some of the crystals also appeared to be modified in the direction of the long axis by prism or dome faces. The measurement of these angles was made on the revolving stage of the microscope, using the cross hairs in the eye-piece as reference lines, and the measured crystals were saved by cementing them to a glass slide with a very dilute solution of gum damar and benzole. Strengite, in very pretty pink botryoidal forms with drusy surface, was noticed occurring with the cacoxenite on limonite from Noble's mine, Bearville, Lancaster Co., Penn.

Mineralogical Laboratory, Columbia College.

6. The Great Barrier Reef of Australia: its Products and Potentialities; by W. SAVILLE KENT. With a chart, 48 photomezzotype plates, 16 chromo plates and many woodcuts. 380 pp. 4to. London, 1893 (W. H. Allen & Co. — This beautiful and interesting volume presents the first results of the work accomplished by Mr. Saville Kent in his study of the Great Barrier Reef of Australia; a work which was made possible through the enlightened liberality of the Queensland Government. The more minute and technically scientific descriptions of the different forms of animal life, which the author has studied, are promised in a later publication. The work now completed presents, in a manner equally satisfactory to the scientific and to the general reader, a vivid picture of the marvellously varied and beautiful life of a coral reef. It also gives an account of the economic importance of much of this life, and discusses in detail the observations which throw light upon the geological origin of coral reefs in general.

The region studied affords an unparalleld field for such an investigation. The Great Barrier Reef of Australia extends for a distance of 1250 miles along the coast of Queensland from Torres Straits to Lady Elliot Island, or from  $9\frac{1}{2}^{\circ}$  to 24° South Latitude. The outer edge of the reef is in some cases only 10 miles from the mainland while in others it is 150 miles and varying between these limits. A reef of such extent presents unique opportunities for the study of all the zoological and geological problems involved.

The attention of the reader is claimed first by the admirable portrayal and description of the beautiful life of the coral reef itself. Never before have those, who have known little of corals but the specimens mounted on the shelves of a museum, had such an opportunity to become acquainted with the living corals and the varied features of the growing reef. The author, skillful with his camera as with his pen, was able to secure many photographs not only of the scenes over the reefs in all their diversity of coral growths and groupings, but also of the expanded corals in their natural positions in the shallow waters. We cannot praise too highly the wonderful perfection with which the photographs are reproduced. To the senior editor they bring back vividly the delightful opportunities afforded him over fifty years ago, when in the U.S. Exploring Expedition under Commodore Wilkes, he studied corals and coral reefs in the Paumotus, Tahitian, Samoan and Fiji Islands. Other plates, not equal in execution to those just mentioned, give colored representations of the coral polyps, sea-anemones, etc. It would be difficult indeed to give any adequate idea of the variety of color displayed in the many kinds of animal life present in these coral gardens. The author's observations have resulted in adding many new genera and species to those previously recorded.

The formation of the Great Barrier Reef as a whole the author refers to a gradual subsidence, in accordance with the theory of Darwin.

In the chapter on the economical value of the living productions, it is stated that the reef-regions afford annually raw material for export to the value of £100,000. The pearl and pearlshell fisheries are of prime importance, and so largely have the shells been gathered that an Act of Parliament has become necessary to prohibit their being taken in an immature state, that is, with a less diameter than six inches across the pearl lining. The author has succeeded in transplanting the young shells to quiet and shady waters where their growth was protected, and the artificial propagation thus shown to be possible may have important results. Another industry is that of collecting and curing the Bêche-de-mer, or sea-cucumber, used by the Chinese as an article of food. It yields an average yearly revenue of £23,000. Another less valuable industry is that of the oyster which yields about £8000 annually. The food fishes also include a large number of recognized value, and others not yet utilized. The number of species of Queensland fish is stated to be nearly 900.

It is not possible to give an adequate impression of the wide general and scientific interest of Mr. Saville Kent's beautiful work. The geological student would derive from its illustrations an idea of the luxuriant growth of limestone-making seas that would be like a revelation to him; and to many the views would appear the more marvelous that all this growth is going on in shallow waters.

7. Amount of water in the soil after a period of severe drought.—M. REISET (Comptes rendus, May 23, 1893) communicates some interesting facts relative to the effect of certain forms of vegetation upon very dry soil. The data are derived from observations made during the year 1887 when the rainfall was 5·87 meters instead of over 9°; the average. In June there fell only  $\cdot 028$  instead of  $\cdot 073$ , and in July barely  $\cdot 033$  against the usual amount of 0.72. From the 4th of June to the 23d of July no rain fell. On the 2d of August, after a second period of drought, five samples of earth were taken from a depth of  $\cdot 15$  to  $\cdot 25$  below the surface, each containing from 8 to 10 kg. of soil, and each was quickly powdered, sifted to take out the pebbles, and placed in a glass-stoppered bottle. Two samples of 10 grams each were subjected to a temperature of  $110^\circ$  to  $120^\circ$  C. with the following results.

Percentage of water.

1.	Under	clover	4.84
2.	66	wheat, about ripe	3.78
3	"	scorched herbage	4.70
4.	"	wheat in full growth	5.04
5.	66	scorched lawn	7.84
6.	66	wheat nearly ripe	3.81

Another observation eleven days later was made on the lawnsoil, no rain having fallen in the mean time. There was found a percentage of 6.80.

A second series of experiments was tried on soil, on the 9th of August, a good crop of wheat having been removed from it on the day before.

~ O + O + O.							
					Percer	ntage of wat	er.
Surface	, at th	e roots	of the	wheat		1.22	
				gravelly		4.95	
66		0.40	"	<u> </u>		9.47	
66	66	0.60 r	ed clay	7		14.12	
66	66	0.80	"			21.81	
"	66	1.00 s	ub-soil	red clay.		26.18	

Still another observation, on soil from which vetch and oats cultivated for fodder had been removed ten days before.

Percentage of water.

		0
$\operatorname{At}$	surface	1.30
"	0.20	6.03
"	0.40	7.87
"	0.60	11.42
"	0.80	12.45
"	1.00 subsoil	14.24

These tables are interpreted by M. Reiset as showing that while lawn-grass is wholly scorched in soil having 6.80 to 7.84 per cent of water, wheat can grow and ripen when there is only 1.22. The very vulnerable point in this conclusion is partially recognized by M. Reiset, who admits that at the time when his observations were made, the wheat was approaching or had reached maturity. Our readers can see that at that moment the wheat plant could get on fairly well with far less water than could the lawn-grass in the park. G. L. G.

8. Nitrification.—M. DEHÉRAIN (Comptes rendus, May 15, 1893) has recently reviewed this important subject, endeavoring to gain some hints as to the possibility of increasing the nitrificative activity of the soil in the spring. He was surprised at the prodigious amount of available nitrogen in soil received by him from diverse sources, and where there had probably been no addition of sodium nitrate as a manure. He at once began experiments on the effects of violent agitation on different soil, acting on a suggestion of Schlæsing that trituration and shaking by distributing the "ferments" might increase the energy. The soils on which he experimented were placed under different conditions: one sample of each being kept perfectly at rest; a second, exactly like the first, was from time to time for about six weeks stirred up very thoroughly and like the other exposed to the open air.

	Sample 1.		Sample 2.		Sample 3.	
	Kept still.	Shaken.	Kept still.	Shaken.	Kept still.	Shaken.
(1)	2	44	2	51	2	71
(1) (2)	3	39	2	46	2	57

These figures are of milligrams of available nitrogen in 100 grams of soil.

Further interesting observations show that the ferments are not equally active at all times even in the same season, and further that the artificial increase in nitrificative activity at the beginning of winter when the useful products may be so easily lost is absolutely prejudicial.

Better appliances than those in use would appear to be demanded by the highest type of effective agriculture, and to this should be added also the selection of the most favorable time for stimulating such activity, namely just when the young plants are ready to utilize the products. G. L. G.

9. The action of the Pyocyanic bacillus on plants. - M. CHARRIN (Comptes rendus, May 8, 1893) presents an account of

his attempt to inoculate a thick leaved *Crassulacea* (Pachyphyton bracteosum) with one of the microbes which cause suppuration in animals. The effects depended largely on the amount of infecting material used; the characteristic tints did not appear where only a drop or two of the matter was employed; where more was taken the destruction of tissue was marked and the characteristic color was pronounced. There was a great accumulation of germs in the tissues, especially the intercellular spaces near the point of insertion, but the cells contained comparatively few. There were noticeable chemical changes in the tissues under observation, especially a diminution in the acidity of the foliar tissue, amounting sometimes to the ratio 225: 120.

By this new and interesting chapter of comparative pathology it appears that in the vegetable as in the animal kingdom the activity of microbes (taken from the anima<sup>1</sup>/<sub>2</sub> depends on quantity as well as quality, and that these organisms utilize their secretions. They have the power of altering tissues, modifying their surroundings and changing the reaction of the liquids in which they act. In the two kingdoms there are many means of defence. In the vegetable world the principal one is the resistance offered by the cell wall to intracellular penetration, but in the plant there is no phagocytic defence. On the other hand the toxines are not effective to any great extent in the case of the plant, in fact this amounts almost to complete immunity. G. L. G.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The John Strong Newberry Fund.—The second joint meeting of the various scientific societies of New York City the Scientific Alliance of New York—was held on March 27, 1893 and "had for its object the honoring of the name and fame of the late Prof. J. S. Newberry." The printed Proceedings of this meeting give the address of Prof. Fairchild, further a number of commemorative letters, a list of Prof. Newberry's scientific writings edited by Prof. Kemp, and finally the report of the Committee on the establishment of the John Strong Newberry Fund for Originial Scientific Research.

The plan, as accepted by the Council of the Scientific Alliance, contemplates the establishment of a fund of not less than \$25,000, the income of which shall be devoted to the encouragement of scientific work in the departments with which Prof. Newberry was identified, viz: Geology, Paleontology, Zoology and Botany. Subscriptions large or small, are solicited and may be paid to the Secretary of the Committee, Prof. N. L. Britton.

2. Cordoba Durchmusterung. Brightness and position of every fixed star down to the tenth magnitude comprised in the belt of the heavens between 22 and 32 degrees of south declination. JOHN M. THOME, Director. Buenos Aires, 1892.—This volume is the 16th of the Cordoba observations, and is the first part of a Durchmusterung Catalogue. It contains 179,800 stars, and is a

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continuation southward of Argelander's and Schönfeld's work. It is to be followed by a second volume during this year, and an atlas of twelve plates. The two volumes and the atlas will cover the belt from  $22^{\circ}$  to  $42^{\circ}$  south declination, and will represent the result of 1,108,600 observations made by Mr. Thome and Mr. Tucker. The star-places are for the epoch 1875.0.

3. Smithsonian Meteorological Tables (based on Guyot's Meteorological and Physical Tables). 262 pp. 8vo. Washington, 1893.—(Smithsonian Miscellaneous Contributions, vol. xxxv, No. 884.) The fourth edition of Guyot's invaluable Tables was published in 1884 not long after the death of the lamented author; the completion of the work being performed by his assistant, Prof. Wm. Libbey. The present volume is one of three which, as stated by Professor Langley, are to supply the place of a fifth edition of these tables; the three parts into which the subject is to be divided being Meteorological, Geographical and Physical. Tables based upon the value of the meter provisionally assumed by the U. S. Coast and Geodetic Survey, (viz: 1 meter = 39.3700 inches, have been made by Mr. George E. Curtis. He has also prepared the entire manuscript and carried the work through the press, and to him therefore the many who will use it are deeply indebted. There are one hundred tables included, thermometrical, barometrical, hygrometrical, etc., and these are preceded by about fifty pages of text descriptive of their use.

4. Forest Influences. 197 pp. 8vo. Washington, 1893. (Bulletin, No. 7, U. S. Department of Agriculture, Forestry Division).— This is a timely presentation and discussion by B. E. Fernow and M. W. Harrington of the meteorological observations on record which bear upon the important influence of forest upon rainfall and climatic conditions in general. Appendices are added on the determination of the true amount of precipitation and its bearing on theories of forest influences by C. Abbe; also on the analysis of rainfall with relation to surface conditions by G. E. Curtis.

5. Ostwald's Klassiker der exakten Wissenschaften Leipzig, 1893. (Wilhelm Engelmann.)—The following are the titles of the volumes recently added to this valuable series:

No. 41. D. Joseph Gottlieb Kölreuter's vorläufige Nachricht von einigen das Geschlecht der Pflanzen betreffenden versuchen und Beobachtungen nebst Forsetzungen 1, 2 und 3 (1761–1766). 266 pp.

No. 42. Das Volumgesetz gasförmiger Verbindungen. Abhandlungen von Alex.
v. Humboldt und J. F. Gay-Lussac (1805–1808). 42pp.
6. Celestial Mechanics.—The editors are informed that Dr. G.

6. Celestial Mechanics.—The editors are informed that Dr. G. W. Hill will deliver a course of lectures on Celestial Mechanics at Columbia College, New York City, beginning about Oct 14th. One lecture will be given each week for thirty weeks. The course is free to all who desire to attend. Further information can be had on application to the department of Astronomy, Columbia College.

7. Blaisdell's Physiologies.—It is announced by Messrs. Ginn & Company, Boston, that they have purchased from Lee & Shepard Blaisdell's Series of Physiologies.

# "YEAR OF JUBILEE!"

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WITH PLATES III, IV.

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Prof. Foote is now traveling through northern New York and Canada and has already secured many choice things which will be mentioned next month. His visit to Middleville, Herkimer Co., in July enables us to offer fine doubly terminated Quartzes at from 5c. to \$1.00.

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THE

## AMERICAN JOURNAL OF SCIENCE

#### [THIRD SERIES.]

## ART. XXIII.—*Fireball of January 13th*, 1893. By H. A. NEWTON. (With Plate III).

1. On the evening of January 13th, 1893, Mr. John E. Lewis of Ansonia, Conn., was engaged in photographing the region of the heavens containing the place of Holmes's comet in hopes of securing a picture of the comet. The camera was strapped to the tube of his telescope, and inasmuch as his telescope was without a clock movement he kept the stars in place by giving by hand the proper right ascension motion to the telescope. The plate was exposed for thirty-three minutes, beginning at 7<sup>h</sup> 19<sup>m</sup> P. M. Mr. Lewis's eye was constantly at the eyepiece of the telescope, so that he was unaware of the passage of a bright meteor across the field of the camera until he developed the plate. The next morning he learned that the meteor, whose flight was thus accidentally photographed, had been seen to cross the sky about 7<sup>h</sup> 30<sup>m</sup> on the evening of the 13th. He announced in the newspapers that he had secured such a photograph and requested observations from those who had been so fortunate as to see its flight. Many responses came to Mr. Lewis and to me from various points in southern New England and southeastern New York. Mr. Lewis has kindly placed the photographic plate and all the letters received by him in my hands for examination and discussion.

2. The plate is 4 by 5 inches in size, and the meteor went nearly centrally across it. The photographed portion of the track was nearly 19° long. Near the center of the plate stars of the 10th magnitude are shown, while near the margin those

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somewhat fainter than the eighth magnitude are in general visible. The disks in the latter case are much enlarged and are not entirely symmetrical. An enlarged reproduction of the track in several portions is given in Plate III.

3. Since we have thus a photographic picture of the meteor's path it seems worth while to put on record quite in detail the statements of the several observers from whom we have been able to secure reports. It should be borne in mind that such observations in the nature of the case have always to be made suddenly, and usually by persons not accustomed to exact observing. As a result the statements are always subject to large probable error, and quite large corrections have to be usually given to some or even to all of the observations if we would make them consistent with each other. The character of the observations is often shown in the language used in describing them. Hence original statements may properly be quite fully recorded.

4. The meteor's path as seen from Boston, Mass.—Miss Clara Binswanger of the Boston Public Library was walking on Columbus avenue (Lat. 42° 20'.5, Long. 71° 4'.9) and saw the meteor in the western heavens falling northward, rather obliquely. The color was a bright green, and it resembled an incandescent electric light in a green glass bulb. Mr. E. W. Abell, at my request, called upon Miss Binswanger and obtained more definite statements. He placed against the window a paper, and laying a ruler against it, asked Miss Binswanger to adjust the ruler to the slope of the meteor track as seen against the sky. Three trials were made, and the results sent to me gave inclinations of 37°, 35° and 27° respectively with the vertical. The meteor disappeared to her by passing behind the edge of a building. Miss B. indicated the height at disappearing as about  $\frac{8}{4}$  of the height of the vertical edge of the building and described the place on the west side of Columbus avenue from which she saw it. . Mr. Abell was able to determine very nearly the place where Miss Binswanger stood, and the building behind which the meteor disappeared. Her description indicates an altitude of about 7° when the meteor passed out of sight behind the building. The edge of the building was about 100 yards distant from her. Mr. Abell's tracing from a city map combined with the known directions of the streets implies that the direction was S. 67° W.

5. As seen from Roslindale, Mass. (Lat. 42° 17', Long. 71° 9').—Mr. Frederick L. Wolkins of Roslindale was sitting by his table in his dining room and saw the meteor cross the southwesterly sky, going downward and northward. Mr. Abell on the 27th of January saw Mr. Wolkins and obtained estimates of the inclination of the path as he remembered it.

From three independent trials he obtained lines inclined  $58^{\circ}$ ,  $63^{\circ}$  and  $68^{\circ}$  with the vertical. The meteor disappeared behind a ridge of land about 400 feet from the house, "at an altitude of perhaps from 5 to 7 degrees." At first Mr. Wolkins thought the meteor fell near him in a swamp beyond the ridge. It had a distinctly bluish color, and moved rather slowly. He compared the size to that of a croquet ball, and did not notice a train.

6. As seen from Hingham, Mass. (Lat. 42° 10', Long. 70° 50').-Mr. Julian L. Noyes says that the apparent path was about along a line drawn from the Pleiades through where Jupiter was on that day. The time was 7<sup>h</sup> 30<sup>m</sup>. "From its start it gradually increased in brightness, and then went suddenly out. Its brightest point was about 25° above the horizon. I turned my head just in time to miss the brightest point, and did not see it break, although it might have done so. Then I saw the remnant continue its course with a very faint, dull, red light to within 5° of the horizon and then go entirely out. When it disappeared it was about 5° south of the west point of my horizon. It took a straight course, except that perhaps at the very last it curved a little downward. It could not have made its appearance much above where Jupiter was at that time. From shadows on windows and other appearances I should say that the portions of the course before the brightest point and after it were equal." Jupiter was at the time about due S.W. at an altitude of 42°; the Pleiades were just east of the Meridian and about 18° from the zenith.

Mr. G. E. Kimball and his son also saw the meteor from Hingham "very near 7<sup>h</sup> 30<sup>m</sup> o'clock about  $\frac{1}{3}$  of the way up the zenith at about due west." It appeared at first like a bright fixed star and suddenly seemed to drop from its place, moving toward the north with a brightening glow.

7. As seen from Concord, Mass. (Lat.  $42^{\circ}$  29', Long. 71° 22').—Mr. Fred. A. Tower of the Massachusetts State Weather Service saw the meteor and gives the time as 7<sup>h</sup> 40<sup>m</sup>, P. M. It was blue in color, and its brilliancy exceeded that of a first magnitude star. He gave the altitude as 70° at appearance, and 25° at disappearance. I requested Mr. Tower to look at the heavens at the proper hour and compare the path as he recollected it, with the constellations. He replied after such comparison, "I should say that it began in the constellation Taurus, and ended in the constellation Aquarius."

8. As seen from Leominster, Mass (Lat.  $42^{\circ}$  31', Long. 71° 44').—Mr. N. Harwood saw it at 7<sup>h</sup> 30<sup>m</sup>. When first seen it was 40 to 45 degrees high in the S.W. It descended in a curve towards the north or northwest and disappeared from

view at an altitude of  $20^{\circ}$  to  $25^{\circ}$ . "When first seen it was small and dim,—when it disappeared it was brilliant, and apparently 4 to 5 inches in diameter. I did not notice it burst in pieces. It seemed to disappear almost instantly, leaving a small trail at the last." In his first letter to me Mr. Harwood gave the altitude when first seen as 25 to 35 degrees.

9. As seen from West Medford, Mass. (Lat.  $42^{\circ} 25'$ , Long. 71° 8').—Mr. Geo. B. Frazar saw the meteor fall for a considerable distance, almost vertically, and go behind a barn 150 feet distant from him. It was very bright and intensely clearly defined. The direction was determined by a pocket compass to be between West and W.S.W.; perhaps nearer W.S.W than West.

10. As seen from Berlin, Conn. (Lat.  $41^{\circ} 38'$ , Long.  $72^{\circ} 46'$ ). —Mr. J. E. Beale, editor of the Berlin Weekly News, as he was going out of his office had his attention suddenly aroused by the brilliant light. Judging by the time that elapsed before he got sight of the meteor he thinks it started northeast of the zenith, and the distance from its starting point to where it exploded must have been fully 90°. The course was about two points south of west and the time about 7<sup>h</sup> 35<sup>m</sup>. It burst without any noise, throwing out five or six globes of colored light similar to a sky rocket. The flight was apparently very slow.

11. As seen from Branford, Conn. (Lat.  $41^{\circ}$  17', Long.  $72^{\circ}$  49').—According to a notice in the newspapers Mr. G. W. Calkins about 7<sup>h</sup> 30<sup>m</sup> saw the meteor cross the sky from S.E. to N.W. Just over the town it exploded and broke into three pieces which probably fell into the Sound. No detonation was heard.

12. As seen from New Haven (Lat. 41° 18', Long. 72° 55'). —Mr. S. W. Glenney saw it in the N.W. at  $7^{h}$  30<sup>m</sup> by his watch. It had a beautiful blue color, and left a long trail of red which resembled sparks. He saw it explode but heard no report. The path had a slight curve with a direct downward course. When it exploded it seemed to him to be very near the earth.

13. As seen from Stratford, Conn. (Lat. 41° 12′, Long. 73° 8′).—Miss Alice E. Curtis says it was of a bright blue color and was going toward the N.W., too far to the west she thought for fragments to have fallen in Connecticut.

14. As seen from Newtown, Conn. (Lat. 41° 25′, Long. 73° 18′).—Mr. John J. Northrop was with a friend driving, and they saw the body just before it broke. It descended in a northwesterly direction, more westerly than north, that is, in the direction of Poughkeepsie, or the Catskill Mountains. They thought that it fell beyond the borders of Connecticut.

15. As seen from near Stevenson, Conn. (Lat.  $41^{\circ} 22'$ , Long. 73° 13').—Mr. G. W. Bradley was driving between Botsford and Zoar with a friend. They saw a flash, looked up and saw the meteor explode, and heard the noise. "In coming over the hills of Zoar it must have nearly touched the trees here." The time was 7<sup>h</sup> 30<sup>m</sup> and they were certain that when it exploded it was not over  $\frac{1}{4}$  mile from them because they heard the report in a few seconds.

16. As seen and heard from Danbury, Conn. (Lat. 41° 23'.7, Long. 73° 28').—Mr. Marcel Foubert observed a flash of light and looking upwards saw a meteor of unusual brilliancy. It left a long luminous trail behind it. When the meteor reached the vicinity of the Pleiades it exploded scattering bright red pieces in every direction. The report of the explosion was very slight, and the interval between the explosion and report was but a few (three or four) seconds. Its direction was northwest.

17. On the 6th of April I went to Danbury and saw Mr. C. R. Curtis, an intelligent farmer living two and a half miles N.W. of Danbury (Lat. 41° 25'.6, Long. 73° 29'). He was startled on that evening by the bright flash of light, looked up and saw the meteor overhead. It was perfectly stationary in the heavens. This want of apparent motion was a surprise to him. For a time it grew in brightness, and then diminished and went out without changing place. The color was at first white, but later was red. The duration of the phenomenon he thought was about 12 seconds. He indicated at my request the time, which by my watch was about 7 seconds.

18. As seen from Bethel, Conn. (Lat. 41° 22′, Long. 73° 25′). —According to the Danbury News Mr. Louis Ohlweiler, of Bethel, heard an explosion like the sound of a pistol shot, though not as loud, directly overhead. Looking in the direction of the explosion he saw five balls of fire spread out like the balls of an exploded rocket. To him the balls seemed about the size of an egg and blue-white in color, like electric lights. He kept the balls of fire in view for three seconds, when they vanished in darkness.

19. As seen from Pawling, N. Y. (Lat. 41° 38', Long. 73° 36').—Mr. J. Frank Smith saw it a little east of south, and its course seemed to be nearly vertical.

20. As seen from near Poughquag, N. Y. (Lat. 41° 43', Long. 73° 41').—Miss Statia C. Brill was driving with other persons. They saw it a little east of south. It seemed to fall somewhere near the mountains about West Pawling. The explosion was accompanied with about as much sound as a rocket would make, barely as much.

21. As seen from Newburgh, N. Y. (Lat. 41° 31', Long. 74° 1').—A gentleman while looking towards the east was attracted by a bright blue light. The roof of a house partly hid the display from him. At first glance it seemed to be nearly stationary and he was almost convinced that it was a piece of fireworks, but on looking again, the rapid shooting of the fiery body obliquely towards the north convinced him that it was a meteor, and the brightest he remembered ever seeing. He would say that it dropped directly east of Newburgh and either on or east of the Fishkill Mountains. Two other observers in Newburgh walking in South street, saw the meteor descend from a point in the east, and fall quite near the Groveville toboggan slide across the Hudson River. It was of a greenish tint, very brilliant, large and beautiful. Another person describes it as of a raspberry hue.

22. As seen from Howell's Depot, N. Y. (Lat. 41° 28', Long. 74° 15').-Mr. James N. Mapes says, that it was almost east of him.

23. As seen from Nanuet, N. Y. (Lat.  $41^{\circ}5'$ , Long.  $74^{\circ}0'$ ). Mr. J. H. Stertzer was walking in a northeasterly direction when he saw the meteor. It began east of the zenith  $65^{\circ}$  to  $70^{\circ}$ high, and broke at a height of about  $45^{\circ}$  and N.E. of the zenith. It appeared to be about the size of a man's head, and its light was equal to that of the full moon. It lasted about one second.

24. As seen from near Rosendale, N. Y.-Mr. C. Veeder was driving (Lat. 41° 53', Long. 74° 5'), and saw the meteor fall in an easterly direction.

25. As seen from New York City.—Mr. William H. Caldwell was in Central Park near the south end of the mall. The meteor appeared to have started a little east of the mall, and seemed to be very near the earth. It had a bluish color with a long tail and was at least five seconds in the sky. "After the tail had disappeared a red ball appeared to fall towards the earth for at least a second and fade slowly out of sight." He thought he heard a slight detonation like a skyrocket. A rough sketch accompanying his letter showed a course of the meteor toward the left, and making an angle less than 45° with the horizon. The mall is directed about N. 16° E.

Mr. Oliver B. Culley was walking along Third avenue between 129th and 130th streets when he saw the meteor. It described an angle with the horizon of about 40° to  $45^{\circ}$ , and broke into fragments of various sizes at the height of about  $25^{\circ}$  or  $30^{\circ}$  above the horizon, and about half way between E. and N.E., or rather more to the east. It had a brilliant blue color. Mr. Henry Hartman saw it from Washington Heights "at an angle of about 45°," and its diameter before bursting seemed about 16 inches. It burst into fragments before disappearance.

26. The Lewis Photograph.—The track which appears on Mr. Lewis's photograph has very clearly marked margins, and part of the way has also a clearly defined central track. The stars near the center of the plate have well rounded figures, and even near the margins of the plate the star figures can be bisected with a fair degree of accuracy. The probable error of position is less evidently than that of the Bonn Durchmüstering places. I therefore selected from the stars near the track six couples of stars, and one isolated star each of which had been observed at Leyden. The couplets were of stars near the track, one on each side of it. No second suitable star was available on the plate for use with the odd star. With a filar micrometer the distances of these stars from the track were measured and the position of the point where the line joining two stars of a set cut the center of the meteor track was computed. This process avoided the necessity of considering the scale value of the micrometer screw, except for the distance of the odd star from the track.

TABLE I, showing the measured positions of seven points on the photographed meteor path, and their distances from a great circle through the extreme points.

No. of	Name of	R. A. of star	N. Decl. of star.	Places of points	in meteor path.	D'viat'n from
	star, B. D.		Leyden, 1875'0.	R. A., 1875 <sup>.</sup> 0.	N. Decl. 1875 <sup>.0</sup> .	G.Circle
1	33°, 273	1h 33m 15*12	33° 42′ 24″·4	1 <sup>h</sup> 33 <sup>m</sup> 15 <sup>s</sup> 12	33° 48′ 20″·0	0".0
2	33.234 33.233	$\begin{array}{cccc} 1 & 20 & 0.26 \\ 1 & 20 & 0.05 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 20 0.15	33 47 57.0	-10.2
3	33, 190 33, 189	1 7 20.97 1 7 9.82	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 7 15.40	33 42 30.6	-23.3
4		0 50 44 79	33 29 38.7	0 49 58.38	$33 \ 27 \ 24 \ 7$	-31.0
5	32.101	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 30 6.62	32 59 11.0	-15.0
6	32.99 32.85	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 25 12.20	32 50 77	-25.3
7	32.80 32.48	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$		32 27 17	0.0
-	32. 42	0 13 10.82	32 40 37.5	0 13 51.91	54 21 11	0.0

In this way were obtained the right ascensions and declinations of seven points on the track. In Table I are given the comparison stars with their places as determined at Leyden. In the fifth and sixth columns are the seven places centrally on the track. Drawing a great circle through the two extreme places and computing the declinations on that circle for the right ascensions of the fifth column, and subtracting these

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from the declinations in the sixth column we have the remainders in the seventh column. These residues, taken strictly, imply that the meteor path was curved a little, the concavity being to the north. But if a great circle is drawn 15'' north of the one already computed as passing through the extreme points it will represent the seven places with extreme deviations of about 15''. This is not greater than the average errors of measurement from the plate as shown by the agreement *inter se* of individual measures. A very slight curvature of path is therefore indicated but is clearly not proven.

27. Possible causes of curvature of path.—The effect of gravity, and that of the rotation of the earth carrying the camera, to produce curvature of path would be in the opposite direction to, and for any reasonable supposition as to velocity would be much smaller than, that indicated by the residuals in column seven. If the meteor's light has the same refraction as that of the stars there would be from this cause a small theoretical curvature of path, since the starlight comes through the whole atmosphere and the meteor-light only through a part of it. But this cause too would furnish residuals very small compared to those of column seven, and they would be opposite in sign. If there is any curvature we may therefore refer it to glancing in the air caused by the atmosphere's resistance of the irregularly shaped body.

28. Time at which the meteor appeared.-A number of the observers say that 7<sup>h</sup> 30<sup>m</sup> was the actual or approximate time of the appearance of the body. These were Mr. Noyes and Mr. Kimball at Hingham, Mr. Harwood at Leominster, Mr. Calkins at Branford, Mr. Glenny at New Haven, Mr. Bradley at Stevenson. Mr. Beale at Berlin says 7.35. Mr. Curtis of Danbury placed it later than 7.30. Mr. Tower at Concord says 7<sup>h</sup> 40<sup>m</sup>. As the time of the 75th meridian from Greenwich is in use in the whole region there is no correction for differences of local time. No one names a time earlier than  $7^{h} 30^{m}$ . Probably there is a slight tendency to name a time which is too late, since the ordinary observer of such a meteor does not at once note the time, being interested in the appearance of the body. Hence it is safe to take 7<sup>h</sup> 30<sup>m</sup> as not far from the true time of appearance. It may easily have been however two or three minutes later.

29. Mr. Lewis's latitude in Ansonia was  $41^{\circ} 20' 40''$ , and his W. longitude  $73^{\circ} 4' 20''$ . Allowing for precession, etc., I find that the plane that passed through Ansonia and the path among the stars as photographed by him cut the earth at  $7^{h} 30^{m}$  in a line which crosses the meridian of  $73^{\circ} 28'$  (that of Danbury) at latitude  $41^{\circ} 25' 9''$ . Each minute of time later than  $7^{h} 30^{m}$ would carry that point of intersection with the meridian of Danbury north  $3'' \cdot 6$  or about 370 feet. The line for  $7^h \cdot 30^m$  crosses centrally the upper Kohanza reservoir as given upon the Danbury sheet of the new map of Connecticut. The plane was at  $7^h \cdot 33^m$  inclined  $10^\circ \cdot 3'$  to the vertical at Ansonia, and the earth's rotation in five minutes would change this inclination by a very small quantity, a quantity, however, so small that it may be safely neglected.

30. The various observations reported in 4-25 when used for computing the meteor's path through the air are of necessity liable to large errors. This is almost universally true for such meteors. The proper adjustment of the unavoidable discrepancies is a matter of some delicacy. No systematic treatment like the method of least squares is feasible. No formal system of balancing the errors, or taking an average seems proper. The difficulties that arise are not those which a mere computer meets with, but are much more like those which a judge encounters when the witnesses give conflicting stories. The judge hears the evidence of all the parties, and then taking into account the way in which witnesses are accustomed to use language, and all the necessary and all the probable relations of the parties and things concerned, works out of conflicting stories what to his mind is the most reasonable statement of the facts.

31. If a meteor's path through the air is regarded as part of a straight line the location of that line is evidently determined by four conditions; or, if the beginning and ending of the body's path are to be found, two more conditions, six in all, are to be fulfilled. Each usable observation taken by itself gives one or more equations and reduces by one, or more than one, the number of remaining conditions. When, however, the observations furnish more equations of condition than the four or six required an adjustment becomes necessary.

In practice I have found it better in collating meteor observations to first select the best observations and use these exactly as made to reduce the number of unknowns to be found. In the present case the photographed track is of course the best observation, and it furnishes two out of the four conditions needed to fix the line of the meteor's motion. The photograph determines a plane through Ansonia and the required line. Relative to the stars the plane is quite exactly determined, the errors being principally such as are caused by errors of the measurements which I made on Mr. Lewis's original slide. The probable error of one measurement I estimated at about three-tenths of a minute of arc. The relation of this plane to the earth's surface, and so to other observers is however further affected as shown above (29) by the uncer-

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tainty of the epoch of the flight, since the earth was rotating relative to the plane passing through Ansonia and the track.

32. Next to the photograph the statements of Mr. Curtis (17) combined with the several statements in 18-25 seem least fitted for fixing one point in the line of the meteor's motion. Mr. Curtis was probably a few hundred feet north of the photographed plane, but he could not have been far from it because by reason of the earth's rotation that plane passed over Mr. Curtis's place between 7<sup>h</sup> 30<sup>m</sup> and 7<sup>h</sup> 35<sup>m</sup>. To Mr. Curtis the meteor seemed perfectly stationary. This was probably not strictly true. We can only assume that the apparent motion was to him not very large. The body was moving at an inclination to the vertical, as will be seen, of 40° or 50°, and when it disappeared was not many miles from him. If the real path continued met the ground much to the east of him, the apparent path seen by Mr. Curtis would have gone down towards the horizon to the east-southeast; if much to the west of him the apparent path would have gone upward nearly vertically, but a little to the south, toward a point south of the zenith. I believe, if the meteor had been directed to a point more than two or three miles either east or west of Mr. Curtis, that he would in the seven seconds, more or less, during which he was watching it have noticed the downward or upward motion of the fireball. I shall assume therefore that the line of the meteor's path met the ground in Lat. 41° 25'.5, Long. 73° 29'. This point I shall call Clapboard Ridge.

33. The reports from N. Y. State, are in accord with and confirm in a general way this assumption.

Mr. Smith (19) sixteen miles N. 23° W. from Clapboard Ridge says that it fell a little east of south.

Miss Brill (20) twenty-three miles N. 28° W. from Clapboard Ridge says it fell a little east of south.

To observers in Newburgh (21) twenty-nine miles N. 77° W. it fell in the east.

Mr. Mapes (22) forty miles N. 86° W. saw it almost east of him.

Mr. Stertzer (23) thirty-six miles S.  $49^{\circ}$  W. says that it broke N.E. of the zenith at a height of  $45^{\circ}$ . Altitudes in such cases as this are usually overestimated. This observation together with those reported from Rosendale and New York City (24 and 25) so far as they are definite are all fairly well represented by the assumption made.

34. We have thus established three out of the four conditions which the straight-line path of the meteor must satisfy, namely, the line must pass through Clapboard Ridge, and must lie in a plane passing through Clapboard Ridge and Ansonia, which plane is inclined to the vertical of either Clapboard Ridge or Ansonia a little more than ten degrees. (The elevations of Ansonia and Clapboard Ridge above the sea may in this case be neglected.) The remaining condition is less exactly determined by the observations. The best unknown to use is the place of the meteor's quit, that is, the point on the celestial sphere from which the meteor was moving.

35. A glance at the observations in and near Boston, and in N. Y., shows that the meteor was moving in that plane at a large angle with the vertical and also at a large angle with the horizon. But no one of the observations has by reason of the position of the observer, or other quality, a clear right to be used to the exclusion of the others.

36. The meteor's path is assumed to be a right line; hence its apparent path to each observer must be an arc of a great circle on the heavens. The true path produced passes through Clapboard Ridge; the circle of its apparent path must contain the point near the horizon in which Clapboard Ridge would be seen by the observer. The apparent path produced backward on the sky must contain the meteor's quit We must determine on the photographed arc a place for the quit such that the various observations shall be best satisfied, regard being had to every known quality of the observations.

37. An artificial globe (celestial or terrestrial) is convenient for the study of the problem. Set the pole of the globe in the zenith, and then the meridians are vertical circles. If the statements of the observers are not definite enough (and they are not in this instance) to make it worth while to consider the different places of the zeniths of the observers, we may treat the pole of the artificial globe as the zenith of each observer. Then, the point on the horizon in the azimuth of Clapboard Ridge from the observer must be in the circle of each observed path. Assume on the photographed path a quit, and suppose arcs drawn from this quit to the several horizon points. If the quit is correct the observed paths were in these arcs. Move the quit up or down the photographed circle until the arcs represent the statements of the several observers with the least violence to the language used. Instead of a globe a stereographic or a central projection of a hemisphere may be If the observations warranted greater refinement of used. treatment methods of computing could be easily devised. I find that if the quit is taken 45° from the line joining Clapboard Ridge to Ansonia the various accounts will be satisfied about as well as if the quit was assumed to be at any other point in the photographed plane.

38. The distance from Ansonia to Clapboard Ridge is twenty two miles and I assumed that the angle at Clapboard Ridge is 45°. The length of the track on the photograph

plate was 18°.8. The place where it entered upon the plate was 72° 7 from the horizon measured in the photographed plane. These data show that at the entrance of the fireball upon the photograph plate it was 17.6 miles from the camera, and at the other margin of the plate it was 15.75 miles dis-The length of the photographed track was five and tant. three-fourths miles. The altitudes above the earth were 16.5 and 12.5 miles respectively. According to the usual hypothesis of the density of the air as we ascend, the barometric pressure at the middle of the photographed track was a little less than two inches, and the pressure was more than twice as much at the lower as at the upper point. The uncertainty in the numbers in this article is not very great. The principal cause of uncertainty is the want of exactness in the location of the quit, and the triangles are so located that this cause cannot largely affect numbers given. The residuals not exceeding  $15^{\prime\prime}$  in (26) that indicate possible curvature correspond to deviations of the path from a plane not exceeding 6 feet.

39. In Plate III is given an enlarged print of the photographed track in six portions. It is about twenty six inches long, so that it represents in length the track on a scale of 1:14000. The breadth of the track in the photograph at the two ends is due to want of exact focus. Owing to changes during the processes of reproduction the print shows the path near its end much narrower than did the original plate. On Mr. Lewis's plate the path shows near the end a clearly marked central line and a smoothly limited marginal region five or six minutes in breadth. The latter is only faintly reproduced in the plate.

40. The stone was evidently single during its passage across the field of view. The breaking up which was noticed by several observers took place lower down.

The irregularities of light in the path increase notably in frequency towards the end of the plate. At first they recur only after hundreds of feet, while near the end they are perhaps ten times as frequent. Such irregularities might be due to small fragments breaking off from the main mass. But it would seem reasonable that in that case we should be able to detect small spurs of light from the path and of these I see no trace. It seems much more reasonable to suppose that the stony mass was in rotation, more rapid at the end than at the beginning, and that unequal amounts of burned material were thrown off according as a well burned or a raw surface was for the instant in front.

#### ART. XXIV.—On a Photometric Method which is independent of Color; by Ogden N. Rood.

THE principle underlying most of the photometric methods now in use depends on a comparison of the illumination of two adjacent fields; in some instances as where a spot or a ring is made to disappear, this idea is thinly disguised, but instantly becomes apparent when the lights are differently colored.

The object of the present paper is to present a mode of procedure in which the coloration of the two surfaces, even though at a maximum of vividness, is a matter of entire indifference, since the process depends not on a comparison of these surfaces, but on the shock which the retina experiences when one surface is quickly withdrawn and replaced by another. If we take a uniform circular disc of any color, illuminate it evenly, and then set it in rotation slowly or rapidly, the retina will receive no shock, since the parts replacing each other in the retinal image are in all respects identical, in other words no flickering will be perceived. If, however, one-half of the disc reflects less light than the other by  $\frac{1}{50}$  of the total amount, with appropriate rates of rotation a faint flickering will be noticed, which will increase in intensity as the difference of the luminosities of the two halves of the disc is made greater.

Accordingly I prepared a set of about a hundred discs of drawing paper, their depth of tint ranging from the whitest white paper down to the blackest, the gradation being as even For the determination then of the reflecting as practical. power, for example of a vermilion disc, it was only necessary to select from the series a gray disc which when combined with it in equal parts gave no perceptible flicker, and afterwards to determine the reflecting power of this gray disc in terms of the standard white cardboard. Results were thus obtained for the principal colors, red and blue-green, yellow and blue, green and purple. The difficulty in measuring the reflecting power of these colored discs was in all cases the same, and was due to the fact that it is hard to obtain gray discs with absolutely uniform surfaces. This trouble, or a lack of uniformity in the colored discs themselves, was to a considerable extent obviated by reversing the halves of the composite disc so as to employ the previously unused surfaces. Small irregularities, texture, or a sandy appearance do not interfere with the use of the discs to a noticeable extent, but when the depth of the tint changes slowly over an extended surface it gives more trouble. Of course the case frequently arose where in the entire hundred discs not one could be found with

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which the flickering entirely disappeared with quite low rates of rotation, and here it was necessary to determine with which gray disc the flicker was at a minimum. This was accomplished by combining the same colored disc with *two* gray discs, a larger and a smaller, on the same axis, when it would become evident which was the more favorable combination, and the observer would notice that the luminosity of the colored disc must be nearer to one gray disc than to its mate, or about equally distant from both.

As before stated results were obtained for six discs, but these were selected so as to be complementary to each other in pairs, and in order to test the process they were now combined pair-wise and the resultant luminosities of their gray mixtures were determined by the old method, and afterwards *calculated* on the basis of the figures furnished by the flickering process.

 $\begin{array}{cccc} & {\rm Gray\ mixture.} & {\rm Diff.} & {\rm Gray\ mixture.} & {\rm Diff.} \\ {\rm Purple\ and\ green} & \left\{ \begin{array}{c} 27\cdot5 \ observed \\ 27\cdot5 \ calculated \end{array} \right. 0 & {\rm Red\ and\ blue-green} & \left\{ \begin{array}{c} 20\cdot2 \ observed \\ 21\cdot1 \ calculated \end{array} \right. 9 \\ 10 \\ {\rm Gray\ mixture.} & {\rm Diff.} \\ {\rm Yellow\ and\ blue} & \left\{ \begin{array}{c} 27\cdot85 \ observed \\ 29\cdot1 \ calculated \end{array} \right. 1\cdot25 \end{array} \right. \end{array}$ 

These experiments were not at all elaborate, and as their greatest difference barely exceeds one per cent of the reflecting power of white cardboard, they may be taken as furnishing a proof of the correctness of the process employed.

Thus far we have dealt with the combination of white (gray) discs with those that are strongly colored, and it remains to give an example of the process as applied to two differently colored but not complementary discs. To test this matter it was necessary to find two colored discs having the same or nearly the same reflecting power. In my collection I finally found two such discs, a cyan-blue with a reflecting power of 23.9 and a purple for which the figure 23.3 had been obtained : these discs when combined gave a scarcely perceptible flicker. Since then, graded series of yellow discs have been made, but it has been impossible to find time to hunt up their equivalents in luminosity and make the necessary determinations.

This flickering process having answered so well, the procedure was reversed, and used with great advantage to facilitate the determinations of the values of the gray discs executed in the ordinary way; in other words the series of gray discs as made by myself is not pure gray but has a slightly yellowish tint that makes estimation on equality of luminosity a little more difficult than it ought to be. Accordingly in measuring the reflecting power of the gray discs by the old method, the standard white and blacks discs were combined with a *small* amount of an orange-yellow disc which made their mixture match the tint of the gray disc under experiment. The luminosity of the orange-yellow disc in terms of standard white card-board being known, the final result was calculated with equal facility and the annoyance removed. It is hardly necessary to add that in all cases the amount of white light reflected from the standard black disc was taken into account.

An experiment was now made to test the flicker process by using it to determine the reflecting power of two gray discs which were afterwards measured in the ordinary way, and the following result was obtained:

Direct determination	34.1	•	29.1
Flicker "	33.7		28.6
Difference	•4		•5

These determinations were not elaborate but may suffice for the purpose.

Afterwards a more careful set of observations was made to ascertain with what minimum difference in luminosity the flicker became insensible ; a series of five light-gray discs was made with gradations so small that these would have required elaborate work for their individual determination which was not attempted, directly, the method of measuring the least and the most luminous disc being employed, and the difference between the figures divided by four. When these discs were tested flicker fashion in pairs, it was found that the intervals between them were not at all identical, one being larger and its neighbor smaller than the average interval, but each pair nevertheless furnished a faint but distinct flicker. If the intervals had been regular, as was intended, the experiments would have proved that with a difference of  $\frac{1}{50}$  part of the total light a flicker could be perceived; as it was, it showed that a considerably smaller difference suffices, probably about  $\frac{1}{100}$ .

It is evident that for the purpose of measuring the reflecting power of colored discs, it will not in every case be necessary to undergo the labor of making an elaborate set of gray discs; if the experimenter is furnished with six or eight brilliantly colored discs, the reflecting power of which has been carefully determined, then, with these and black and white discs, he will be able to match new discs and measure their luminosity in the old way.

There does not seem to be any reason why this process with the aid of well known optical devices should not be applied to ordinary photometric work, or to such as is carried on in the interior of the observing telescope of a spectroscope. In simple work with discs like that here presented, the flicker photometer is necessarily on the model of a stair case, and the transitions though small are always abrupt; but when there are other modes of regulating the illumination this would not be the case, and the advantage of multiplying observations would be more fully experienced. Some experiments for dividing up even the interval between two discs have been begun, with promising results, but are not yet finished.

It is well known that gazing steadily at a flickering surface is trying to the eyes, but in the operations above described no inconvenience whatever from this source was experienced, since if the flicker was strong a glance revealed the fact and another disc was substituted; the faint flickering which demands more prolonged attention seems to be no more trying to the eyes than ordinary optical work.

It may be a matter of some interest in physiological optics to know that the sensation called "flickering," is independent of wave-length and connected with change in luminosity. When two differently colored surfaces of the same luminosity are successively presented to the eye as above described, no shock is experienced, and the colors are seen to mingle in a soft streaky way; if observation is prolonged for some time, subjective effects begin to manifest themselves especially with quite low rates of rotation; it is of course best not to study these with undue curiosity.

Columbia College, June 19th, 1893.

ART. XXV.—Actinolite Magnetite Schists from the Mesabé Iron Range, in Northeastern Minnesota; by W. S. BAYLEY.

ATTENTION has been repeatedly called to the existence of beds of amphibole schists associated with the ores in the older iron regions of the Lake Superior District. Brooks,\* Wichmann<sup>+</sup> and Wright<sup>+</sup> referred to those occurring in Wisconsin under the name actinolite schists and anthophyllo-actinolite schists, and Julien under the name tremolite-schists. Those

<sup>\*</sup> T. B. Brooks: Geol. of Wisconsin, vol. iii, 1873-79, p. 525, 577, 578, etc.

<sup>†</sup> A. Wichmann: 1b., vol. iii, p. 639, etc. ‡ C. E. Wright: 1b., vol. iii, p. 699, etc.

A. A. Julien: Ib., vol. iii, p. 226, etc.

found in Michigan have been called anthophyllite schists by Brooks and Brush\* and by Julien.+ In the Penokee district of Michigan and Wisconsin, Irving and Van Hise<sup>+</sup> describe them as actinolitic and magnetitic slates, and mention them as forming a portion of the iron-bearing member, just below the upper fragmental slates and immediately above the similarly fragmental vitreous quartzites of the Penokee series. They are associated with slaty and cherty iron carbonates and with ferruginous slates and cherts, regarded as chemical sediments.

Lane and Sharpless§ have recently shown that in some of these schists from the Marquette area the amphibole is rich in iron and magnesium, while entirely devoid of even a trace of calcium, and hence that it should be classed with the variety grünerite.

The relations of these schists to the other members of the iron-bearing series have been made out only in the Penokee area as above stated, though they are said by Irving and Van Hise to be intimately associated with cherty carbonates in the Animikie rocks of Minnesota.

The widespread occurrence of these peculiar rocks throughout all of the iron bearing horizons of the Lake Superior region that have been subjected to more than a merely superficial examination, must be of significance. Consequently the discovery of them on the newly opened Mesabé Range is of some interest from a theoretical, if not from a practical standpoint. The object of this note is simply to announce this discovery and to describe very briefly the characteristics of the rocks.

The easternmost end of the Mesabé area is in the vicinity of T. 61N. R. 12 W. Minnesota. In the S.E. 1 of the S.E. 1 of Sec. 34 in this town, and only half a mile from the north side of the great gabbro mass lying to the south, is a series of dark, heavy schists highly charged with magnetite. Of these eight specimens have been examined, the geological associates of which are unfortunately not known. Under the microscope it is seen that these rocks consist almost exclusively of magnetite and an almost colorless amphibole.

The magnetite forms from fifty to ninety per cent of the entire rock-mass. It occurs as large and small grains imbedded

\*T. B. Brooks and G. J. Brush: Geological Survey of Michigan, vol. i, 1869-1873, p. 114.

A. A. Julien: Ib., vol. ii, 1873. p. 24, 91-93, etc.
A. A. Julien: Ib., vol. ii, 1873. p. 24, 91-93, etc.
R. D. Irving and C. R. Van Hise: The Penokee Iron-bearing Series of Michigan and Wisconsin, 10th An. Rep. U. S. Geol. Survey, p. 389.
S. A. C. Lane and F. F. Sharpless: this Journal, xlii, p. 505, 1891.
R. D. Irving and C. R. Van Hise, l. c., p. 404.
T. Winchell: The Mesabé Iron Range, Geol. and Nat. Hist. Survey of Minn. 20th Ann. Rep. 111.

Minn., 20th Ann. Rep., p. 111.

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in the amphibole. The smaller grains, with the exception of the tiny dust particles scattered through the amphibole, all show traces of octahedral or cubic faces. The larger grains are very irregular in outline, but their irregularity is due rather to the agglutination of tiny grains with crystallographic contours than to the accumulation of masses with accidental boundaries. Traces of octahedral faces may be seen in nearly all of the large magnetite masses, and in some cases these latter appear to be sections of well developed crystals.

The amphibole is in large colorless plates that interlock by irregular sutures, or in sheaf-like bundles of tiny fibers. In the former case the mineral includes magnetite so thickly that in the hand-specimen the rock appears finely granular; but it reflects light evenly from large areas, and these upon close inspection are learned to be the cleavage faces of the amphibole. In cross section the plates sometimes present well marked crystallographic outlines in which the prismatic planes of hornblende are plainly distinguishable, and these sections are crossed by two cleavages cutting each other at the hornblende angle of 124°. In other sections only a single cleavage is apparent as a series of parallel lines against which the extinction is about 14°. The double refraction of the mineral is fairly strong and is negative, and the plane of its optical axes is parallel to the single cleavage. In two of the sections studied many of the plates are crossed by polysynthetic twinning lamellæ as in the case of the grünerite described by Lane and Sharpless.

The fibers in the sheaf-like bundles are colorless like the material of the plates or are very light green. Their extinction is sometimes parallel to their long axes and sometimes is slightly inclined to them. Their double refraction is somewhat stronger than that of the plates and their polarization colors are usually very brilliant. Their axes of least elasticity are nearly parallel to the longitudinal directions of the needles which are therefore negative, if the orientation of their optical axes is as it is in normal hornblende. Two cleavages are discernible, one parallel to the long directions of the fibers and one (a parting) transverse to them. Cross sections of the bundles were not seen.

The properties of the plates and of the fibers sufficiently characterize both as a tremolitic or actinolitic hornblende or as grünerite.

A second amphibole intergrown with the colorless variety differs from this latter only in having a greenish tinge. It may also be slightly more strongly doubly refracting, but otherwise it is similar in all respects to the colorless mineral. An analysis of one of the best examples of these schists, No. 8779, from S.E.  $\frac{1}{4}$  of S.E.  $\frac{1}{4}$ , Sec. 34, T. 61, N. R. 12 W., Minn., yielded Mr. W. H. Melville the following figures :

	No. 8779.	No. 8784.
SiO <sub>2</sub>	12.35	1.16
TiO <sub>2</sub>	.12	none
$Al_2 \tilde{O}_3$	·10	1.81
$\operatorname{Fe}_{2}O_{3}$	58.68	69.08
FeÖ	21.34	27.10
MnO.	1.22	.33
CaO	1.91	•53
MgO	4.08	.25
Na <sub>2</sub> O	tr.	
$P_2 \tilde{O}_5$	·25	•06
Loss	.19	
Total	100.24	100.32

This is a rock composed exclusively of large plates of the colorless amphibole and large grains of magnetite. The latter mineral was not analyzed, but a rock from near No. 8779, consisting of almost pure magnetite was analyzed by Mr. Melville, who reports the results entered under No. 8784. Neither the magnetite in 8779 nor that in 8784 contains any notable quantity of titanium, and thus they differ markedly from the gabbro magnetites bordering much of the south side of the Mesabé range.

With respect to the amphibole in this rock it is manifestly impossible to decide positively whether it is grünerite or actinolite. If we regard the Fe<sub>2</sub>O<sub>2</sub> as existing in the magnetite, and ascribe to this component also the MnO, half of the MgO and sufficient FeO to satisfy the formula Fe<sub>2</sub>O<sub>4</sub>, there remain the other oxides, after deducting enough CaO to combine with the P<sub>2</sub>O<sub>5</sub> in apatite, in the following proportions :

$SiO_2$	$\mathrm{Fe_2O_3}$	$Al_2O_3$	FeO	CaO	MgO	Total
71.63	·92	•58	5.80	9.40	11.60 =	= 99.93

which are nearer those of actinolite than of any other amphibole, although the percentage of SiO, is abnormally large.

One specimen, No. 8783, consists of several alternating light and dark bands. Of the latter it need only be said that their composition is similar to that of the actinolite magnetite schists, i. e. they are composed of large plates of amphibole thickly strewn with grains of magnetite. The dark bands pass gradually into the light ones, the magnetite decreasing in quantity as the borders of the light bands are reached, until in the interiors of these bands all of this mineral has disappeared.

#### 180 H. L. Wells—Double Salts of Lead Tetrachloride.

The principal components of the light bands are actinolite of the platy form, grains of a light green amphibole that may be a more ferriferous actinolite, and a few ragged grains of plagioclase. None of these constituents have sharp outlines. They all dovetail into one another even more irregularly than do the minerals of a granitic rock. In the little interstices that sometimes occur between the larger individuals and included within these in considerable quantity are many small and more or less rounded grains of a colorless mineral, whose isotropic sections show the straight bar of a uniaxial interference figure. Other sections are rhomboidal in shape. These are doubly refracting and they extinguish parallel to the diagonals of the rhomboids. The general aspects of the mineral, and its properties, so far as they can be determined, are those of quartz.

The descriptions above given agree very closely with those given by Irving and Van Hise\* for the corresponding schists in the Penokee series, except that in the Minnesota rocks quartz is rare and hematite is absent. The presence of these peculiar rocks in the Mesabé range is noteworthy, since their origin in certain other districts is supposed to be very closely connected with the origin of the iron ores with which they are associated. If in the Mesabé district they are found to be related genetically with an original carbonate of iron, an important analogical link between the Mesabé and the Penokee series will have been established.

#### ART. XXVI.—On some Double Salts of Lead Tetrachloride; by H. L. WELLS.

THE existence of lead tetrachloride has long been surmised from the fact that the corresponding oxide, when dissolved in cold hydrochloric acid, gives a yellow solution in which sulphuric acid does not give an immediate precipitate. Lead tetrachloride itself, however, has never been isolated, nor has any double salt which it forms been satisfactorily described.

Sobrero and Selmi<sup>+</sup> found that when chlorine is passed into a solution containing sodium chloride and lead chloride, the liquid becomes yellow. They found it impossible to isolate the compound either by evaporation or cooling, so that they determined the lead, sodium and chlorine in such a solution, and found it to contain these constituents in the ratio corresponding to PbCl<sub>4</sub>+9NaCl. Sobrero and Selmi say that per-

> \* R. D. Irving and C. R. Van Hise: l. c., p. 389-393. + Ann. Chim. Phys., III, xxix, 161,

haps this is the formula of the compound, but they put a question-mark after it. Their analysis indicates the existence of PbCl, in combination with NaCl, but if the solution had contained a compound of that composition, which was stable with water, it probably could have been isolated by evapora-The fact is that the double salts of lead tetrachloride are tion. not stable with water, as will be shown in the present article. Therefore, since a large excess of sodium chloride must have been present in the solution of Sobrero and Selmi, their analysis could not have determined the composition of the double salt that it contained.

Nicklès\* saturated a strong solution of calcium chloride with lead chloride and chlorine and analyzed the solution. He found it to contain lead, calcium and chlorine in the proportions represented by PbCl<sub>4</sub>+16CaCl<sub>2</sub>. In conclusion Nicklès does not claim that any such double salt exists, but merely claims to have indicated the existence of PbCl.

In view of the fact that the formulæ PbCl, +9NaCl and PbCl<sub>4</sub>+16CaCl, merely represented the composition of solutions, it is remarkable that they are given in some handbooks of chemistry as real chemical compounds. It may be mentioned that Carnegiet has used the formula PbCl, 9NaCl in support of a theory on double halides.

O. Seidel<sup>‡</sup> mentions unsuccessful attempts to isolate PbCl<sub>4</sub> and its double salts with the chlorides of other metals.

Fishers dissolved lead peroxide in hydrochloric acid and found that all the lead in the solution was precipitated again as peroxide by the addition of sodium acetate. He was evidently not aware of the fact that Rivot, Beudant and Daguin had shown, long before, that lead is completely precipitated as peroxide by the addition of sodium acetate and chlorine to its solutions. Fisher found that two atoms of chlorine were used (as would be expected) in precipitating one atom of lead as peroxide. His conclusion that his experiments showed the existence of lead tetrachloride has, apparently, little foundation.

More recently, Ditte¶ has made some experiments on the solubility of lead chloride in solutions containing hydrochloric acid and chlorine. He apparently does not believe in the existence of lead tetrachloride, for he does not mention the compound, while he explains the precipitation of lead peroxide, when such solutions are diluted, by saying that lead chloride is partly dissociated by the act of solution, that the solution then contains oxide of lead, and that this is peroxidized by the

<sup>‡</sup> Jour. pr. Ch., II, xx, 205, 1879 Ann. Mines, V, iv, 239, 1853.

+ Am. Chem. Jour., xv, 10. 1893.

- § Jour. Chem. Soc., xxxv, 282, 1879. ¶ Ann. Chim. Phys., V, xxii, 566, 1881.

<sup>\*</sup> Ann. Chim. Phys., IV, x, 323.

oxides of chlorine formed when chlorine is passed into the solution.

Nikolukine has succeeded in isolating double salts of lead tetrachloride with ammonium and potassium chlorides. He showed that these compounds contain lead and extra chlorine in the proportion required for PbCl<sub>4</sub>, but there is no evidence in the abstracts of his article<sup>\*</sup> that he determined the composition of the double salts. His original article in Russian is not accessible to me. Nikolukine prepared the compounds by dissolving lead dioxide in concentrated hydrochloric acid in sealed tubes, and adding the alkaline chlorides to the solutions thus produced. He describes the double salts as having a lemonyellow color, and states that they are pretty stable, the ammonium chloride compound being decomposed at 120°.

The present investigation has been undertaken with the view of determining the composition of the salts which Nikolukine discovered, and especially in order to investigate the corresponding rubidium and cæsium compounds, which, from analogy, were expected to be more insoluble and stable than the potassium salt. As a result, it has been found possible to prepare the whole series in a state of purity, and the expectations in regard to the easy preparation of the rubidium and cæsium salts have been fully realized. The following salts are to be described:

(NH<sub>4</sub>)<sub>2</sub>PbCl<sub>6</sub> K<sub>2</sub>PbCl<sub>6</sub> Rb<sub>2</sub>PbCl<sub>6</sub> Cs<sub>2</sub>PbCl<sub>6</sub>

These salts are all yellow, and they all crystallize in the isometric system with an octahedral habit.

These salts show a new relation between lead and other metals of Mendeléeff's group IV, with which this type is very common, especially among the double fluorides. It is to be noticed also that this type is almost invariable among the double salts which tetrahalides form, for platinum, iridium, osmium and palladium give analogous, isomorphous compounds, while, as has been recently shown by Dr. H. L. Wheeler of this laboratory, tellurium gives an extensive series of octahedral salts of this type. The octahedral form of the anhydrous salts of this type is very characteristic, and it seems to be universal, except among the fluorides.

All of the lead salts to be described are decomposed by water with the formation of lead peroxide. Chlorine is usually set free at the same time. It may be assumed that two successive reactions take place, which may be represented by the following equations:

\* Berichte, xviii, 370, 1885; Jour. Chem. Soc., I, 123.

(1)  $PbCl_4 + 2H_2O = PbO_2 + 4HCl$ 

(2)  $PbO_{2}^{*} + 4HCl = PbCl_{2}^{*} + Cl_{2} + 2H_{2}O$ 

The extent to which the second reaction takes place depends upon the dilution and the temperature. If the amount of water present is not too great, a state of equilibrium is reached when a sufficient amount of alkaline chloride, hydrochloric acid and chlorine have gone into solution, and the decomposition stops. The cæsium salt is more slowly decomposed by water than others. All the salts are decomposed by boiling with an excess of hydrochloric acid, but the decomposition of the cæsium compound is remarkably slow, especially in solutions containing much cæsium chloride.

When free chlorine is present the cæsium salt is almost completely insoluble in strong solutions of cæsium chloride and in hydrochloric acid. Although the rubidium salt is considerably more soluble, the difference is not great enough so that a quantitative separation can be made. It will be shown in the following article that cæsium can be approximately separated from potassium, sodium and lithium by this means, and that when rubidium is also present the cæsium can be approximately determined indirectly.

The salts to be described can be washed with hydrochloric acid containing chlorine. They are perfectly stable on exposure to the air. When heated in capillary tubes the ammonium salt begins to whiten at about 225°, the potassium salt at about 190° and the cæsium and rubidium salts at about 280°. This temperature for the decomposition of the ammonium salt is about 100° higher than that given by Nikolukine. It is probable that difference is due to a typographical error.

Attempts were made to prepare corresponding sodium and calcium salts, without success.

In analyzing the salts, lead was separated and weighed as sulphate, and, in the filtrate from this, the alkali-metal was determined as sulphate. To determine chlorine, a separate portion was decomposed by a solution of sodium arsenite and chlorine was determined in this as usual.

Ammonium-Plumbic Chloride,  $(NH_4)_2PbCl_6$ :—In preparing this salt, Nikolukine's method of using sealed tubes was found to be unnecessary. A solution of lead tetrachloride was made by adding slightly diluted hydrochloric acid to an excess of lead dioxide at 0°. This solution was quickly filtered through asbestus, and a saturated, cold solution of ammonium chloride in dilute hydrochloric acid was added until an abundant, yellow, crystalline precipitate was produced. The salt was pressed on paper, and then air-dried.

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	Found.	Calculated for $(NH_4)_2PbCl_6$ .
Ammonium	44.61	7.90 45.39
Chlorine	** 0*	45.71

Potassium-Plumbic Chloride,  $K_2PbCl_s$ :—Chlorine was passed into a solution saturated with potassium chloride, lead chloride and hydrochloric acid at 0°, without producing the double salt. Nikolukine has stated that the salt is soluble in an excess of potassium chloride, and, acting upon this suggestion, another solution was made, like the former except that no potassium chloride was used. On mixing about equal volumes of the two solutions and letting the mixture stand at 0° for several hours, a well crystallized crop of the yellow doublesalt was obtained. The air-dry salt was analyzed.

	Found.	Calculated for K <sub>2</sub> PbCl <sub>6</sub> .
Potassium	15.30	15.70
Lead	41.91	41.55
Chlorine	42.49	42.75
	99.70	100.00
Loss on heating	15.07	Cl <sub>2</sub> 14.25

The above method of preparation gives a small yield, and it would probably be better to use a method analogous to that by which the ammonium salt was prepared.

Rubidium-Plumbic Chloride,  $Rb_*PbCl_*$ :--When  $65^{g}$  of rubidium chloride were dissolved in  $250^{cc}$  of water with  $4^{g}$  of lead chloride, no precipitate was produced by saturating the solution with chlorine, but, on adding an equal volume of concentrated hydrochloric acid to this solution, an abundant, yellow, crystalline precipitate was produced. This was collected on a filter, washed with hydrochloric acid containing chlorine and air-dried.

	Found.	Calculated for Rb <sub>2</sub> PbCl <sub>6</sub> .
Rubidium	28.62	28.93
Lead	34.98	35.03
Chlorine	35.85	36.03
	99.45	100.00
Loss on heating	12.41	$Cl_{2}$ 12.01

A solution 35<sup>cc</sup> in volume, made of equal volumes of concentrated hydrochloric acid and water, and containing '0619<sup>g</sup> of rubidium and double the theoretical quantity of lead chloride was saturated with chlorine. A precipitate of the double salt was produced, which, after standing several hours was collected upon a Gooch filter. The rubidium in this precipitate was determined and found to amount to  $\cdot 0318^{\text{g}}$ . One cubic centimeter of the solution dissolved, therefore,  $\cdot 003^{\text{g}}$ of the lead salt, equivalent to  $\cdot 00086^{\text{g}}$  of rubidium. The experiment was made at about 20°.

Cæsium-Plumbic Chloride,  $Cs_2PbCl_a$ :—This salt is very readily prepared by passing chlorine into solutions containing lead chloride and a large excess of cæsium chloride. When hydrochloric acid is present, the excess of cæsium chloride is unnecessary, but in that case the precipitate is very finely divided. The precipitate begins to form in solutions that are nearly at a boiling temperature. A crop obtained without the use of hydrochloric acid was analyzed. It was washed with hydrochloric acid containing chlorine and air-dried.

Cæsium Lead Chlorine	Found. 38•51 30•05 30•99	Calculated for Cs2PbCl <sub>6</sub> . 38.78 30.17 31.05
Loss on heating	99·55 10·96	100.00 Cl <sub>2</sub> 10.35

The salt usually has a lemon-yellow color, but, when very strong hydrochloric acid is used and a large excess of lead chloride is present the precipitate has a dark brown color. Such a crop gave the following analysis:

		Calculated for
	Found.	$Cs_2PbCl_6.$
Cæsium	38.19	38.78
Lead	29.64	30.12
Chlorine	31.35	31.05
	-	
	99.18	100.00
Loss on heating	11.09	Cl <sub>2</sub> 10.35

This is evidently the same compound as the lemon-yellow salt. The cause of the brown color is not known. The presence of lead dioxide in it does not seem probable on account of the strong acid that was used, and, moreover, experiment showed

that this oxide was instantly dissolved by the mother-liquor. It was suspected that this was a dimorphous form of the compound, but Mr. Louis V. Pirsson, who has kindly made a microscopic examination of both products, has found that both are isometric and octahedral in habit. He noticed that while the yellow salt forms perfect octahedrons, the brown compound occurs in octahedral



groups composed of combinations of the cube and octahedron. The accompanying figure, by Mr. Pirsson, shows the prevailing habit of these crystals. The groups are very small, usually not over  $0.015^{\text{mm}}$  in diameter.

Sheffield Scientific School, March, 1893.

#### ART. XXVII.—On a Method for the Quantitative Determination of Casium, and the Preparation of Pure Casium and Rubidium Compounds; by H. L. WELLS.

SINCE no method has heretofore been devised for the accurate quantitative determination of cæsium in the presence of both rubidium and potassium, some experiments have been made in order to test the availability of the plumbic chloride, described in the preceding article, for this purpose. The results have not been as accurate as could be desired, but the method will be useful until a better one is found.

The solubility of  $Cs_2PbCl_6$  in a hydrochloric acid solution (fuming acid diluted with water 1:1), containing twice the theoretical amount of lead chloride and saturated with chlorine, was determined by making a precipitation of about 1<sup>g</sup> of  $Cs_2PbCl_6$  under these conditions in 350<sup>cc</sup> and determining the cæsium in the filtrate. The whole filtrate gave  $0.0119^g$  of  $Cs_2SO_6$ , which corresponds to a solubility of  $0.000068^g$  of  $Cs_2PbCl_6$  in 1<sup>cc</sup>. A similar experiment in which concentrated hydrochloric acid was used, and also a larger excess of lead chloride, gave a solubility of  $0.000049^g$  of  $Cs_2PbCl_6$  in 1<sup>cc</sup>. It has been shown in the preceding article that the solubility of  $Rb_2PbCl_6$  is  $0.003^g$  in 1<sup>cc</sup> under similar conditions.

Some actual determinations of cæsium were made as follows: Known quantities of  $Cs_2PbCl_6$  and about an equal weight of PbCl<sub>2</sub> were dissolved in hot HCl (1:1). Chlorine was passed into the solutions until they became cold, and, after standing about three hours, the precipitates were collected in porcelain Gooch crucibles and washed with hydrochloric acid containing chlorine. The precipitates were decomposed with hot water and the cæsium in the resulting solutions was determined as sulphate. In one case a comparatively large amount of potassium chloride was present. The details are as follows :

	Cs₂PbCl₀ taken.	KCl taken.	Volume 1:1 HCl.	$Cs_2SO_4$ found.	Deficiency as Cs <sub>2</sub> SO <sub>4</sub> .
$\mathbf{A}$	$\cdot 1674^{ m g}$		$35^{\circ\circ}$	·0856	.0026
В	·1592		35	.0807	•0031
С	.1280	0.2 g	35	•0638	·0035

These results indicate greater errors than were expected from the previous solubility determinations. It is suspected that a little of the precipitate was dissolved by washing, and the use of hydrochloric acid containing lead chloride as well as chlorine would probably diminish the error. The last experiment shows that the presence of a considerable amount of potassium has no influence upon the result.

The determination of cæsium by this method can be simplified by weighing the precipitated cæsium-plumbic chloride directly. The salt is perfectly stable at 100°. The following table gives the details of a number of determinations made in this way. The precipitates were all thoroughly washed with hydrochloric acid containing chlorine and dried on an asbestus filter at 100°.

	Cs <sub>2</sub> PbCl <sub>6</sub> taken.	PbCl <sub>2</sub> taken.	KCl taken.	Volume HCl.	Cs <sub>2</sub> PbCl <sub>6</sub> found.	$Cs_2PbCl_6$ lost.
			taken.	•		
Α	$\cdot 2761^{ m g}$	$0.25^{g}$		28°° 1:1	$\cdot 2650^{ m g}$	·0111g
В	.0878	1.0	0.2 g	52 1:1	•0833	.0035
С	·1202	1.0		52 1:1	.1071	.0131
D	.7558	0.1		28 conc.	.7369	·0189
$\mathbf{E}$	·2483	0.1		20 conc.	$\cdot 2359$	.0124

The results show considerable losses in cæsium, which apparently do not entirely depend upon the volume in which the precipitation is made. It is believed that the losses occur chiefly in washing, for large quantities usually show a larger total loss than small ones.

When cæsium and rubidium are together, the precipitation of cæsium plumbic chloride is accompanied by a partial precipitation of the rubidium, unless the quantity of the latter is small. It is possible, however, to make an indirect determination of the cæsium in such a precipitate by weighing it and afterwards determining the weight of the cæsium and rubidium sulphates. Two experiments have been made on this plan, where not only rubidium, but also potassium, sodium and lithium were present.

	A	В
Cs <sub>2</sub> PbCl <sub>6</sub> taken,	0.3261g	0·1545g
Rb PbCl, taken,	0.2845	0.4101

To each of these were added about  $0.15^{\text{g}}$  each of potassium and sodium chlorides,  $0.25^{\text{g}}$  of lithium carbonate and  $0.1^{\text{g}}$  of lead chloride. The substances were dissolved by boiling with dilute hydrochloric acid, about an equal volume of concentrated acid was added, and chlorine was passed until the solutions became cold.

	A	В
Volume of solution,	30°°	$50^{\rm cc}$

After standing several hours the precipitates were collected on asbestus filters in porcelain Gooch crucibles, washed with dilute hydrochloric acid saturated with chlorine, dried at 100° and weighed.

> A B Cs<sub>2</sub>PbCl<sub>s</sub> and Rb<sub>2</sub>PbCl<sub>s</sub> found, 0.5621 0.4538

The precipitates were treated on the filters with hot water, the resulting solutions were evaporated with sulphuric acid, the lead sulphate was removed by filtration, the filtrates were evaporated and finally ignited in an ammoniacal atmosphere and the mixed sulphates were weighed.

Cs<sub>2</sub>SO<sub>4</sub> and Rb<sub>2</sub>SO<sub>4</sub> found, 0'2826 0'2164

For calculating the results, the following formulæ were used :

 $(P = weight of Cs_{2}PbCl_{e} + Rb_{2}PbCl_{e})$ (S = weight of Cs\_{2}SO\_{4} + Rb\_{2}SO\_{4}) Weight of Cs = 5.095S - 2.301P Weight of Rb = 2.006P - 3.801S

	A	В
Cæsium taken	0.1381	0.0599
Cæsium found	0.1464	0.0584
Error in cæsium	0.0083 +	0.0012-
Rubidium taken	0.0823	0.1186
Rubidium precipitated	0.0534	0.0876

The results show that approximate determinations of cæsium can be made by this method when all the alkali-metals are present. The process leaves a part of the rubidium with the potassium, and these two metals can be precipitated as platinic chlorides and their amounts determined indirectly.

The method which has been described is useful for the extraction of cæsium and rubidium from their natural sources. The following method of procedure may be suggested, supposing all the alkali-metals to be present as chlorides in a concentrated aqueous solution :

At least an equal volume of concentrated hydrochloric acid is added, and any precipitated sodium and potassium chlorides are removed. The solution is diluted somewhat to avoid a subsequent precipitation of these chlorides, a solution of lead chloride, made by boiling lead oxide with a large excess of hydrochloric acid, is gradually added while chlorine is passed into the solution until it is cold and until fresh additions of lead chloride fail to produce a yellow precipitate. According to my solubility determinations, this precipitation leaves less than 1<sup>g</sup> of rubidium and a much smaller quantity of cæsium in each liter of the solution. The precipitate is usually almost free from potassium. To ensure the complete purification of the cæsium and rubidium, the precipitate is washed with hydrochloric acid containing chlorine and lead chloride, then it is treated repeatedly with small quantities of boiling water until completely decomposed, and the resulting solution is subjected to a repetition of the foregoing process. The mixed plumbic salts are decomposed with hot water and the resulting, filtered solution is evaporated to dryness to remove hydrochloric acid. The residue is dissolved in hot water,\* the lead is precipitated by the addition of a slight excess of ammonium sulphide and the precipitate is removed by filtration. The solution is evaporated to dryness and the residue consists of cæsium and rubidium chlorides and some ammonium chloride.

The following directions for the separation and purification of the cæsium and rubidium do not involve any new methods, but the course of procedure has been arrived at after a considerable amount of experience, and it may be of use to others. It is assumed that rubidium is more abundant than cæsium in the mixture. If cæsium predominated it would be more advantageous to extract that metal first by an obvious modification of the process.

The mixed chlorides of rubidium and cæsium are dissolved in at least five parts of concentrated nitric acid and the solution is evaporated to dryness and heated until the excess of nitric acid is removed. The residue is dissolved in a small amount of water, and as much oxalic acid as corresponds to twice the weight of the original chlorides is added. The whole is evaporated to dryness and the residue is ignited in platinum until the oxalates are completely converted into carbonates.<sup>+</sup> The carbonates are dissolved in water, the solution is filtered and exactly neutralized with a measured solution of tartaric acid, as much more tartaric acid as has been used for the neutralization is added, and the solution is evaporated until it becomes saturated while hot. The solution on cooling deposits acid rubidium tartrate, which is washed with a small quantity of water and is recrystallized two or three times from a hot saturated solution in the same way until it gives no cæsium spectrum.<sup>‡</sup> The united mother-liquors from the acid rubidium tartrate are evaporated to dryness and ignited in platinum. The resulting carbonates are converted into chlorides, and, to a solution of these in a small volume of 1:1 hydrochloric acid, a solution of antimony trichloride in the same acid is

<sup>\*</sup> No part of this residue should be thrown away on the assumption that it is lead chloride, for the salt  $CsPb_2Cl_5$  is difficultly soluble and resembles  $PbCl_2$ .

<sup>&</sup>lt;sup>+</sup> This method of converting alkaline chlorides into carbonates is due to J. L. Smith, this Journal, II, xvi, 373.

<sup>‡</sup> This method is due to O. D. Allen, this Journal, II, xxxiv, 367.

added as long as a precipitate forms.<sup>\*</sup> The precipitate is collected on a filter and washed with hydrochloric acid. To remove traces of rubidium, the precipitate is thoroughly decomposed with successive, small quantities of hot water, then hydrochloric acid and a little antimony trichloride are added to the whole in order to repeat the precipitation. The last precipitate is washed with hydrochloric acid. It usully shows no rubidium when tested with the spectroscope. The cæsium antimony chloride is decomposed with hot water and hydrogen sulphide is passed into the resulting solution. The filtrate from the antimony sulphide gives, on evaporation, pure cæsium chloride. The filtrates from the antimony double salt are freed from antimony, evaporated to dryness and the mixture of cæsium and rubidium chlorides, which should be very small in amount, is preserved for use in subsequent purifications.

Sheffield Scientific School, April, 1893.

#### ART. XXVIII.—On some Peculiar Halides of Potassium and Lead; by H. L. WELLS.

In a preceding article I have described a series of double chlorides of the type M. PbCl., where M is NH., K, Rb and Cs. It has seemed desirable to extend the investigation by attempting to prepare bromides and iodides corresponding to these salts. A thorough search has been made, using the metals of the potassium group and sodium, with the result that no double bromides or iodides containing extra halogen could be prepared except in the case of potassium. It is remarkable that the potassium-lead bromide and iodide which have been discovered do not correspond in composition to the chlorides. The failure to prepare double salts of rubidium and cæsium corresponding to the new potassium compounds was unexpected, for, as a general rule, the insolubility and stability and the consequent ease of preparation of such compounds become greater from potassium towards cæsium. The explanation of the anomaly probably lies in the fact that extremely concentrated rubidium and cæsium solutions containing a lead halide and the corresponding halogen cannot be obtained, in the case of the bromides and iodides, on account of the slight solubility of cæsium triiodide, and of the double halides which are formed with PbBr, and PbI.

The compounds to be described probably have the composition represented by the following formulæ:

\* Method of Godeffroy, Berichte, vii, 375.

K<sub>3</sub>Pb<sub>2</sub>I<sub>8</sub>.4H<sub>2</sub>O K<sub>3</sub>Pb<sub>2</sub>Br<sub>8</sub>.4H<sub>2</sub>O

These formulæ may be also written,

#### 3KI.2PbI, I.4H, O and 3KBr.2PbBr, Br.4H, O.

The composition of these salts is very remarkable on account of the small amount of the extra halogen that they contain. They apparently do not correspond to any other chemical compound that is known.

The Iodide,  $K_s Pb_2 I_{s'} 4H_2 O$ : — This salt forms brilliant, black, prismatic crystals, sometimes a centimeter or two in length and three or four millimeters in diameter. Although the crystals have fine prismatic faces, they never appear to have definite terminations. The ends usually appear fibrous, as though made up of numerous small crystals in parallel posi-When the crystals are crushed on paper it is evident tion. that they enclose much mother-liquor. The salt is deposited from nearly or quite saturated solutions of potassium iodide containing lead iodide and iodine. It is deposited at ordinary temperature, usually slowly, after the lapse of several hours or even after several days. In preparing the compound, the lead iodide and the iodine can be varied considerably, but it is formed only in very concentrated potassium iodide solutions and it is difficult to obtain crops of it which are not evidently contaminated with this salt in the form of crystals. The salt is stable in the air but it is instantly decomposed by water or alcohol, so that it cannot be washed.

Six separate crops have been analyzed, and great care has been used in selecting them and in drying them on paper for analysis. In two cases the product was rapidly and finely pulverized during the drying operation, but without any effect upon its composition. The results of the six analyses agree with remarkable closeness, but in spite of this fact it must be assumed, from considerations which will be given subsequently, that all these products were seriously contaminated with potas-The fibrous nature of the crystals and the consium iodide. centration of the mother-liquor make the possibility of such a contamination very evident, but the constancy of this contamination, as indicated by the uniformity of the analyses, is very remarkable in view of the fact that some of the products were made at wide intervals of time, covering a period of about six months, so that there were considerable variations in the laboratory temperature.

The products were made under the following conditions :

	KI	$PbI_2$	I	Volume.
А	$450^{ m g}$	$30^{ m g}$	$15^{ m g}$	?
В	425	30	50	450 <sup>cc</sup>
С	445	40	70	470
D	445	40	100	470
$\mathbf{E}$	445	40	150	460
$\mathbf{F}$	200	15	15	200

They gave the following results on analysis:

	K	Pb	I	$H_2O$
$\mathbf{A}$	9.31	22.03	64.00	4.69 = 100.03
В	9.25	22.30		4.81
С	9.07	22.03	63.98	4.89 = 99.97
D	9.21	21.98	64.09	4.71 = 99.99
E	9.20	22.13	64.17	
$\mathbf{F}$	9.27	22.02	63.84	

In these analyses and those which follow, water was determined by weighing it directly in a calcium chloride tube. The other determinations were made according to the methods mentioned in the preceding article on the double salts of lead tetra-chloride.

The above analyses correspond closely to the formula  $K_{9}Pb_{4}I_{1,0}.10H_{2}O$ , but it will be shown beyond that the probable formula of the pure compound is  $K_{9}Pb_{2}I_{0,2}.4H_{4}O$ . This requires K=7.25, Pb=25.56, I=62.74 and  $H_{2}O=4.45$ . If this is the true composition, it must be assumed that all of the analyzed products were contaminated with about 16.5 per cent of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt.

It is to be noticed that the products were prepared under great variations in the amount of iodine present, and it can be safely assumed, from the care with which the products were examined, that they were not contaminated with the salt KPbI, 2H,O nor any similar compound. The amount of lead iodide in the solutions was comparatively small, and a large part of it was used in forming the salt under consideration, so that any contamination must have been chiefly potassium iodide. It is therefore evident, since the salt is not decomposed on exposure, and since the analyses show a constant amount of extra iodine in spite of the variations of this ingredient in the solutions, that the analyses must show the true ratio between the lead iodide and the extra iodine in the pure compound. This ratio is  $2PbI_{a}$ :I in both  $K_{a}Pb_{a}I_{a}$  and  $K_{a}Pb_{a}I_{a}$ .

The Bromide,  $K_s Pb_2 Br_s AH_2 O$ :—This compound forms dark brown, prismatic crystals which are solid and definitely terminated, so that they do not have the tendency to hold inclosed mother-liquor which the iodide has. The salt is easily prepared and it crystallizes well, but it is extremely unstable. When exposed to the air it begins to whiten almost instantly, giving off bromine. It is stable, however, in air containing a considerable amount of bromine vapor, so that it can be dried by pressing on paper in such an atmosphere. It is sufficiently stable, when corked up in a weighing-tube, to be rapidly weighed in a cold room without serious decomposition.

Three crops of the double bromide were analyzed. A and B were made, in each case, by adding  $20^{cc}$  of bromine to  $400^{cc}$  of a cold solution which was saturated with potassium bromide and lead bromide and allowing the mixture to stand over night. C was made like the other crops, except that  $30^{cc}$  of bromine were used.

	А	Found. B	С	Calculated for K <sub>3</sub> Pb <sub>2</sub> Br <sub>8</sub> .4H <sub>2</sub> O
Potassium	10 33	10.41	10.24	9.43
Lead	32.02	31.90	32.49	33.30
Bromine	51.96	52.15	52.05	51.48
Water		5.59	5.28	5.79
		100.02	100.06	100.00

The analyses agree with the formula as well as could be expected, considering the instability of the compound. The analyses show almost exactly one atom of extra bromine for two atoms of lead, so that the compound is closely related to the iodide if not exactly analogous to it.

The satisfactory crystals of the bromide and the stability of the iodide suggested the possibility that, if the two compounds were really analogous as suspected, isomorphous mixtures of the two could be made which would retain the desirable qualities of both, so as to be solidly crystallized and stable enough to be accurately analyzed. Experiments showed that isomorphous mixtures could be readily obtained which crystallized satisfactorily, and it was found that even small amounts of iodine had the effect of greatly increasing the stability of the compound. It was noticed that when a product was made from a solution containing free bromine and iodine in nearly atomic proportions (BrI), an almost perfectly stable, bright red salt was obtained. The color of this salt is far from being intermediate between that of the black iodide and the dark brown bromide, but, since the analyzed products contain about 23 atoms of bromine to one of iodine, it does not seem probable that any definite relation between the two halogens exists. It is remarkable that such a small proportion of iodine should have so great an influence upon the color and stability of the product, but it is to be noticed that only one eighth of the

AM. JOUR. SCI.-THIRD SERIES, VOL. XLV, NO. 273.-SEPT., 1893.

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halogens in these compounds is in excess, so that, if all the iodine is in this condition it amounts to about one-third of this excess.

The crops A and B had a dark bronze color. They were successive crops made by adding bromine to a strong solution of potassium iodide containing lead iodide. The exact conditions are unknown, but it is probable that insufficient bromine was used to set free all the iodine which the solution contained. These products were apparently as stable as the iodide.

C and D were successive crops made by continuing the addition of bromine to a somewhat similar solution until a change of color showed that the free iodine had been converted into BrI. These salts were red. An analysis of the mother-liquor from D gave, KBr = 31.3,  $PbBr_2 = 1.8$ , Br = 6.7, I = 8.3,  $H_0O(difference) = 51.9$ .

E was made by adding 31<sup>g</sup> of bromine to 430<sup>g</sup> of the abovementioned, analyzed solution. This crop was also red, but it was not quite as bright in color and not as stable as the others. On continuing the addition of bromine, still less stable crops were obtained which approached the pure bromide in color. These were not analyzed.

The analyses of the five crops are as follows:

	K	$\mathbf{Pb}$	Br	I	$H_2O$
Α	9.41	31.57	41.40	12.06	5.09 = 99.53
В	9.24	31.55	39.27	14.57	
$\mathbf{C}$	9.90	32.88	48.66	3.40	5.24 = 100.08
D	9.99	32.74	48.70	3.30	5.02 = 99.75
$\mathbf{E}$	10.24	32.26	49.97	2.07	

The ratios calculated from the above analyses are as follows :

	K	:	$\mathbf{Pb}$	:	$\operatorname{Br} + I$	:	$H_2O$
Α	1.57		1.		3.99		1.83
В	1.55		1.		3.99		
$\mathbf{C}$	1.59		1.		4.00		1.82
D	1.61		1.		4.00		1.76
E	1.68		1.		4.16		

The ratio required for the formula K, Pb, (Br,I), 4H, O is,

1

K	:	$\mathbf{Pb}$	:	$\operatorname{Br}+\operatorname{I}$	:	$\mathrm{H}_{2}\mathrm{O}$
1.50		1.		4.		2*

The analyses agree well with this formula, except that the water is somewhat low. Although  $3\frac{1}{2}$  molecules of water would correspond more closely to these analyses than 4, the latter number is considered more probable on account of the fact that the analyses of the iodide show some excess over four molecules.

### J. Trowbridge—Oscillations of Lightning discharges. 195

It is to be seen that these mixed salts correspond in composition to the bromide. The analogous mode of formation of the iodide, the identical relation of the lead to the extra halogen in the iodide and the other products, as well as the existence of these mixed salts, make it appear certain that the analyzed iodide was invariably impure and that the pure compound should be considered as analogous to the other salts. This view has been confirmed by a crystallographic examination of the iodide and the red bromo-iodide, which Prof. S. L. Penfield has kindly undertaken. He has found that both these salts crystallize in prisms of the tetragonal system. Unfortunately the crystals of the iodide were without terminations, so that a more detailed comparison of the two salts could not be made.

The nature of these peculiar salts is not clear. If they are, strictly, hydrous "double salts," such higher halides as  $Pb_2I_s$  or  $K_sI_4$  must be assumed. If they are formed from such compounds as  $PbI_4$  or  $KI_3$ , they must be considered as hydrous triple salts.

Sheffield Scientific School, April, 1893.

# ART. XXIX.—On the Oscillations of Lightning discharges and of the Aurora Borealis; by JOHN TROWBRIDGE. (With Plate IV.)

It is well known that when air is subjected to a sudden strain at the moment of an electrical discharge it acts like glass or a similar elastic solid and is cracked in zigzag fissures : indeed the resemblance between the ramifications of lightning and the seams produced in plates of glass by pressure has been commented upon by various observers. Photographs of powerful electric sparks lead one to conclude that a discharge of lightning makes way for its oscillations by first breaking down the resistance of the air by means of a disruptive pilot spark; through the hole thus made in the air the subsequent surgings or oscillations take place.

In examining the early photographs of electric sparks by Feddersen one perceives indications that the electric oscillations tend to follow for at least some hundred thousandths of a second the path made by the pilot spark; and there are observers who believe that by rapidly moving a camera they have obtained evidence that successive discharges of lightning follow the same path. Professor Lodge has protested, with reason, against the conclusions drawn from the method of "waggling" the head or camera: for the movement of the head or camera certainly requires the hundredth of a second while the discharge of lightning is over in less than one hundred thousandth of a second.

The method of the photography of electrical discharges by means of a revolving mirror seems to be the best method of studying the behavior of air suddenly subjected to the electric strain. I have therefore examined this behavior with more powerful means than those employed by previous observers; and it may be well to recall here the fact that usually in lightning discharges, high electromotive force and great quantity are frequently combined in a very short interval of time. The modern alternating machine and the device of the transformer enables one to study the character of lightning more successfully than is possible by means of an electrical machine: for both the electromotive force of the discharge and its quantity can be adjusted over a wide range. In my study of this subject I employed an alternating machine giving from three hundred to four hundred alternations per second, with a current from fifteen to twenty amperes, and the photographic apparatus was the same as that which was used in my investigation on the damping of electrical oscillations on iron wires.\* By means of a step-up transformer and an oil condenser, discharges of high electromotive force and great quantity could The method of the excitation of a be readily obtained. Ruhmkorf coil or transformer by means of an alternating dynamo, due originally to Spottiswode, has placed in the hands of the experimenter, as I have said, powerful means of studying electrical discharges.

Since my object was to study the photographs of sparks having both great electromotive force and great quantity I limited myself to discharges of about two centimeters. Bv the device of an air blast and other contrivances for obtaining a quick break in the continuity of the electrical discharges, Professor Elihu Thompson has shown how sparks of many feet in length can be obtained. Figures 1 and 2 are reproductions from untouched negatives not enlarged, and ten to twelve oscillations can be counted on each photograph. The interval between the oscillations is about one hundred thousandth of a second; and it will be noticed that the electrical discharge follows exactly the same path in the air for three hundred thousandths of a second. During this length of time every sinuosity in the air path is exactly reproduced. I employed terminals of tin; and on figure 1 it will be noticed that a mass of melted and vaporized tin remained suspended in the air for at least three hundred thousandths of a second before it was dissipated in a comet-like tail. During the three hun-

\* Phil. Mag., Dec., 1891.

dred thousandth of a second, therefore, the air remained passive while the electrical oscillations took place. During this time it is fair to conclude that the heat produced by the passage of the spark was not sensibly conducted away. If conduction of heat had taken place the electrical resistance of the air path would have been sensibly altered and the path of the discharge would have changed in form. Here I think we have an interesting limit to the time it takes atmospheric air to respond to the phenomenon of heat conduction.

I have said that the discharges I employed were powerful both in regard to electromotive force and to quantity. Iron terminals one-quarter of an inch in diameter were raised to a white heat by the continuous passage of the sparks and globules of the melted metal were formed. When the sparks were passed through the secondary of a transformer of about thirty seccohins of self induction, three fifty-volt Edison lamps placed in multiple in the primary of the transformer, which consisted of merely two layers of thick wire, were lighted to full incandescence. The spark from two large glass condensers of 5000 electrostatic units each, excited by an electrical machine, passed through the same step-down transformer barely raised a six-volt lamp to a red heat. The study of the efficiency of step-down transformers in thus transforming transient currents of high potential to transient currents of low potential and comparatively large current enables one to obtain an estimate of the high potential of lightning and of the current which accompanies its fall of potential. Thus if C denotes the current in the lightning discharge and E the electromotive force, C' and E' the corresponding quantities in circuit of the primary of the step-down transformer and A the efficiency of the transformer we shall have

#### C'E' = ACE

The element of time and the mode of transformation must be considered in any estimate of the amount of energy in lightning discharges. Although a powerful spark of electricity from two Leyden jars each of 5000 electrostatic units is incapable of decomposing water directly; yet by its passage through the secondary of a suitable step-down transformer it can decompose the water in the primary with great evolution of gases, and it is probable that an ordinary discharge of lightning of a few hundred feet in length could light, for an instant, many thousand incandescent lamps if it were properly transformed by means of a step-down transformer. Indeed the ringing of electrical bells and the melting of electrical fuses are of common occurrence during thunder storms and manifest the energy of lightning discharges. During a recent visit at a

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summer hotel which was lighted by incandescent lamps, I was much interested to observe that the lamps blinked at every discharge of lightning, although the interval which elapsed between the blinking and the peals of thunder showed that the storm was somewhat remote. This effect was doubtless due to induction produced by the surging of the lightning discharges. On the occasion of a heavy discharge the lights were completely extinguished, although no fuse was burned. My observation of this effect of lightning upon electric light circuits also leads me to believe that the system of carrying electric light wires along gas fixtures where both gas fixtures and electric light fixtures are combined is fraught with great danger. If there is a leakage of gas at the joints of the gas pipes or through a sand hole in the casting of the pipes electric sparks arising through resonance effects or from ordinary passage to earth of an electric charge brought into the building by the electric wires can ignite the escaping gas and produce a mysterious conflagration. Such a conflagration was averted in the hotel in which I noticed the blinking of the lamps only by the careful scrutiny of an attendant who noticed a jet of gas from a pin hole in the gas fixtures impinging on the wood work. During the storm a minute electric spark had ignited the escaping gas. Electric light wires and gas pipes should never be contiguous; for no lightning guard or protector can ensure that minute sparks, due in some cases to resonance effects, may not arise.

The study of the disruptive or oscillatory discharge of lightning is closely connected with that of the brush discharge and that of the phenomenon of the Aurora Borealis; for the disruptive discharge if it is an oscillatory discharge ceases to be disruptive after a few hundred thousandths of a second, as figures 1 and 2 show, and partakes of the nature of a brush discharge. The zigzag fissures in the air disappear and only the spark terminals glow. Recent experimenters have exhibited, as a marvel, the lighting of a vacuum tube through the human body by grasping one terminal of a suitable transformer with one hand and by holding the vacuum tube in the other hand. It must be remembered, however, that the lines of force proceed from the hand which holds the vacuum tube through the air and the walls or floor of the room to the other terminal of We can change this brush discharge or the transformer. luminosity at either terminal of a transformer into a disruptive discharge by lessening the distance between the terminals or by increasing the electromotive force.

I am fully aware that the oscillatory discharge of lightning with its disruptive effects I have noted—its permanence of path and the fading of the disruptive discharge into the brush discharge or mere luminosity at either of the spark terminals, is a far simpler phenomenon than the luminosity produced in rarefied tubes; for in the latter phenomenon we have the dissociation and impact of molecules, and we must consider all the problems of atomic motion in addition to those of the oscillatory nature of electrical waves. It is not my purpose to enter into a consideration of the molecular movements involved in oscillatory discharges in vacuum tubes; but having discussed some of the general features of discharges of electricity in air at the ordinary pressure I shall endeavor to trace the connection between such discharges and the phenomenon of the Aurora Borealis. To my mind the luminosity in a vacuum tube held in one hand while the other hand grasps the terminal of a Ruhmkorf coil, closely represents the phenomenon of the northern light, for we have in this case a dischargeof electricity from a higher level to a lower through a rarified Although in this paper I restrict myself to a discus medium. sion of the general relations between discharges of lightning and the phenomenon of the Aurora Borealis, and do not enter into a study of the molecular movements excited by electrical discharges, I am impelled to devote a few words to the subject of the stratified discharge and to show that it has no connection with the oscillatory discharge of electricity such as we The distances between the stratifications do are considering. not seem to be changed by modifying the period of forced oscillation given to the transformer over a wide range. I have produced the stratifications by employing an interrupter of a Ruhmkorf coil giving from sixty to one hundred vibrations per second, and by the use of two alternating machines, one giving 300 to 400 alternations per second and the other 900 to 1000 alternations per second. The distances between the stratifications do not seem commensurate with the rate of alternation of the exciter of the transformer. On the other hand the distance between the stratifications is not dependent upon the amount of self induction in the circuit. In one case quadrupling the self induction reduced the distance between the stratifications one-half. This reduction was due not to the increased self induction but to the increased resistance; for the introduction of a water resistance of some megohms diminished in a similar manner the distance between the stratifications. In short I could not discover any connection between the law  $t = 2\pi \sqrt{\text{LC}}$  and the phenomenon of stratification.

I have said that we can pass by insensible gradations from the condition of the brush discharge to that of the disruptive discharge. By intercalating a non-inductive water resistance and a vacuum tube between the terminals of a suitable transformer we can exactly imitate the phenomena observed when

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the vacuum tube is held in one hand while the other hand grasps one terminal of the transformer. In this case the water resistance takes the place of the resistance of the air of the room. The intensity of the discharge being thus much diminished one can readily study various manifestations of stratification which may perhaps be termed transitory stratifications in distinction to the stationary wave-like forms observed in narrow tubes. The transitory stratifications can be produced at will by touching suitable points of a vacuum tube with the finger or by connecting such points with the ground. Such stratifications are stationary as long as the ground connection is maintained, and are independent of the rate of the alternating machine which excites the transformer. It is evident that the condenser action of the vacuum tube plays an important part in this phenomenon. In observing the striæ and waving columnar form of the light excited in this manner in tubes filled with rarefied gases, one is led to believe that the stratified form of the Aurora Borealis is produced in a similar manner. Fig. 3 is a form of the northern light Let us suppose that a discharge of elecnoticed by me. tricity takes place in rarefied air between A and B, and that C is a region of cloud or moisture. C can be regarded as the finger or earth conductor which is applied to the tube of rarefied air and which seems to throw the discharge into transitory stratification, and to give the waving form of the Northern light.

The pulsation, therefore, of the Aurora Borealis is in no way, I believe, connected with any oscillatory discharge; yet certain writers have intimated that the glowing of vacuum tubes which are connected with one terminal of a transformer and the light of the Aurora is due to millions of electrical oscillations per second. Now it is impossible to study the question of the rate of oscillation of the brush discharge, by means of Federsen's method for the light of the discharge is not sufficient to produce a photograph. A brief consideration, however, of the laws of electrical oscillations shows, I think, that such writers are mistaken. The rate of decay of the amplitude of such oscillations is expressed by the well known factor

 $\frac{\mathrm{R}t}{2\mathrm{L}}$ 

#### $\mathbf{E}$

Now in the case of a brush discharge R is enormously large. A resistance of thirty or forty ohms was sufficient to completely damp the oscillations of the sparks studied by me in the research on the damping produced on iron wires. In the case of the brush discharge although we may be dealing with very small values of self induction and small values of time, we have on the other hand great values of R. I believe therefore that the brush discharge is reduced to the case of one throb which is analogous to the pilot spark in disruptive discharges. In regard to the Aurora, it may be urged that the resistance of the rarified air is not enormous. In answer to this, it can be said that the phenomenon of the Northern light can be best reproduced by intercalating a tube of rarefied air with some megohms of a water resistance between the terminals of a suitable transformer. The supposition that the Northern light is produced by the action of extremely rapid electrical oscillations on molecules of rarefied air is not borne out by the theory of transient currents and experiment shows that the phenomenon of the waving and apparent stratification observed at times in the Aurora is due to the re-distribution of the lines of force which is produced by suitable earths in the shape of regions of cloud and moisture.

The comparatively small resistance of the electric spark in air noticed by many observers is due I believe to the permanence of path, for this path is intensely heated and is practically a charred hole in the air. When this path no longer becomes such a hole and the heated air rises and is dissipated, the oscillations of the electric spark become rapidly damped, and we have the phenomenon of the glow at each of the spark terminals without the disruptive discharge; that is, we perceive what is termed a brush discharge. The lines of force crowding from one terminal seek through the air of the room the other terminal, and in passing through rarefied air the energy along the lines of force is manifested by molecular actions which are apparently protean in form. I see therefore no evidence for believing in the rapid oscillation of the Aurora.

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# ART. XXX.-The Auriferous Veins of Meadow Lake, California; by WALDEMAR LINDGREN.

General type.—Fissure veins containing auriferous sulphides and arsenides with gangue of tourmaline, quartz and epidote in granitic and diabasic rocks.

By far the larger part of the veins of the gold belt of California have a gangue of quartz alone or quartz with some

dolomite or calcite,\* contain free gold besides sulphides, and occur in the sedimentary auriferous slate series or in the eruptive bodies, unaltered or dynamo-metamorphosed, which are connected with them; the large granitic areas are usually barren. The group of veins to be described here shows thus a type which in many respects differs from the ordinary. Indeed, auriferous deposits of this class do not appear to have been mentioned as occurring in any other part of the United States.

Location and discovery.—The Meadow Lake mining district is situated in Nevada County about ten miles north of Cisco, a station on the Central Pacific Railroad at elevations ranging from 7000 to 7500 feet. The first divide of the Sierra Nevada whose summits here reach 9000 feet, is only eight miles distant towards the east. The climate is severe and snow sometimes falls to a depth of twenty feet on the level. A rough trail leads into the district from Cisco; a wagon road thirty-five miles long leads to Truckee by a circuitous route.

The mines were discovered in 1863 by H. H. Hartley, and a great rush took place to the district in 1865 and 1866. The free gold found at the surface soon gave way to relatively poor sulphides and the boom speedily collapsed. At various times subsequently some work had been done on the principal mines and only recently the deposits have been subject of some discussion in the technical papers. Considering the difficulties of access and climate, there is some doubt as to whether any of the deposits can ever be worked with profit. The ores will not average more than from seven to ten dollars per ton at the most. Probably \$200,000 or \$300,000 have been expended in the district, while it is doubtful if more than \$75,000 have been taken out.

General Geology.—The area shown in the sketch map (p. 204) is of a rough mountainous character, the elevations ranging from 5,800 to 7,800 feet. The vegetation is scant, the soil having been swept away by the Pleistocene ice sheet once covering the region, leaving enormous bare expanses of the prevailing granitic rock.

Granodiorite.—A light gray granitic rock occupies the larger part of the area of the map and in it is contained nearly all of the veins. The rock is in general identical with the gray so-called granite that occupies such large areas in the

<sup>\*</sup>In a footnote in an article on "The Gold deposit at Pine Hill" (this Journal, August, 1892) regarding gold in calcite and dolomite I omitted to mention that such occurrences had first been noted by Prof. W. P. Blake from Mariposa and Amador Counties, Cal. Annot. Catal. on the principal mineral species of California." Sacramento, 1866.

Sierra Nevada and which probably extend through southern California far down into the peninsula of Baja California \*

The rock consists in typical development of feldspar, quartz, biotite and hornblende with medium grained hypidiomorphic structure. The soda-lime feldspars are usually considerable and to a variable extent in excess of the alkali feldspars. The silica varies between 60 and 73 per cent; the amount of lime is variable, but it rarely exceeds while it usually falls somewhat short of the sum of the alkalies. While in some varieties which cannot be distinguished from the others in the field, there is more potash than soda, a frequently occurring relation is 2 per cent Ka<sub>2</sub>O to 4 per cent Na<sub>2</sub>O. It will be seen that the rock very closely approaches some quartz-mica-diorites and often might be indicated by that name.<sup>†</sup>

This term, however, besides being clumsy, does not sufficiently express its close relationship to granite, brought out by its frequently high percentage of silica and low percentage of lime, by its variable percentage of alkali feldspars and by the muscovite sometimes occurring in it. On the Survey maps of the Gold Belt of the Sierra Nevada, of which district Mr. G. F. Becker is geologist in charge, it has therefore been determined to indicate this rock as *granodiorite*, which term it is hoped will find general acceptance.

Age of the granodiorite — The granodiorite is later than the quartzitic slates of Signal Peak or Red Mountain north of Cisco, which have been extensively metamorphosed by it. As these sedimentary rocks are the direct continuation of the series which a few miles farther south at Sailor Cañon have been identified as Jura-Trias from the meagre fauna occurring in them, the granodiorite evidently postdates that period.

At Meadow Lake several interesting facies of the granodiorite occur. Near the diabase contact it appears darker and more basic by increasing hornblende. West of Meadow Lake from the Keystone mine up towards French Lake there is no biotite, but at many places a monoclinic pyroxene appears and the rock contains abundant titanite. At several places near French Lake a peculiar augite-diorite occurs composed of quartz, plagioclase and augite; the areas of this rock, connected by transitions with normal types, are distinguished by the brilliant white color of the glaciated outcrops.

*Diabase.*—An area of diabasic rock occupies the eastern margin of the map, adjoined on the west by dark basic diorite. It is sometimes, as at Meadow Lake dam, rather a uralitized

\* Compare: Petrographical notes from Baja California; W. Lindgren. Proc. Calif. Acad. Sci., 2d series, vol. i, Part II, 1888.

+ It is also closely related to the Tonalite of Mount Adamello, but it did not for several reasons seem advisable to adopt that name.

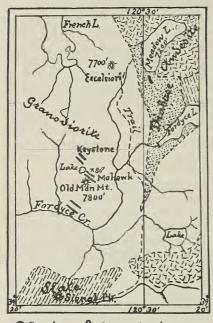
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## 204 W. Lindgren-Auriferous Veins of California.

diabase-porphyrite; at Fordyce dam, farther south, it is a biotite-diabase. The relations of the diabase to the granodiorite are not clear beyond doubt, but the latter appears to be the younger rock.

Andesite.—Several small masses of andesitic breccia of late Tertiary age cover the older rocks to the west of Meadow Lake; north and east of it large masses of this volcanic rock appear.

Ore deposits.—The granodiorite area contains between Signal Peak and Meadow Lake a great number of black veins



Meadow Lake and vicinity, Scale 2 Miles = 1 Inch.

and seams composed of quartz, tourmaline and epidote, together with grains and smaller masses of pyrite. In certain places the latter mineral, and other sulphides have been formed to a large extent and are auriferous enough to render their exploitation possible. A few of the veins which have been worked from time to time are indicated on the figure. The strike is northerly or northwesterly, the dip vertical or at high angles to the northeast; the width of the veins is variable; sometimes, as at Excelsior, it reaches twelve feet. The walls are frequently indistinct. The veins near Meadow Lake do not seem to be traceable for long distances, while some of those of Old Man Mountain,

which is a rounded granitic dome, traversed in several directions by fissure systems, appear to be continuous for half a mile or more. The country rock is not extensively altered in the vicinity of the veins. Many small veins occur at the contact of granodiorite and diabase near Meadow Lake and a few are also found in the latter rock just south of the lake.

Ores.—The ores consist of iron pyrite, arsenical pyrite, pyrrhotite, zincblende, and rarely galena; on the decomposed surface much coarse free gold occurred which, however, was soon replaced by the sulphides mentioned and in which the gold occurs in extremely fine distribution.

Auriferous copper ores prevail at the Keystone, with cuprite, chrysocolla and other secondary minerals. At the most developed mine, Excelsior, iron pyrite is the most abundant ore. Silver does not occur to any notable extent in the ores.

Gangue.-While some white quartz with admixed sulphides occur, the usual gangue is a black, hard and dense rock of sometimes almost basaltic appearance, in which the ores are disseminated.\* In more coarse-grained specimens yellow epidote, quartz grains and small radiating aggregates of a dark brown tourmaline are visible. Under the microscope the black veinstone is resolved into an interlocking aggregate of quartz grains, occasionally traversed by cracks along which comminution and crushing has taken place; gas and fluid inclusions are plentiful; epidote and sometimes zoisite form aggregates in places; tourmaline occurs as irregular grains with the quartz but much more commonly as slender crystals and radial aggregates intimately and plentifully imbedded in The tourmaline has pleochroic colors varying the quartz. from bright brown to dark bluish or greenish gray. Skeleton crystals are common, the interior being filled with quartz grains and bunches of radial chlorite. This latter mineral is quite common in some slides, sometimes traversing the tourmaline in small veins. Brown mica occurs in aggregates, together with the tourmaline. A colorless mica, titanite, ilmenite and some calcite were also observed. The ores occur intimately intergrown with this gangue. In one case pyrite was observed surrounded by a ring of pyrrhotite.

In a small vein occurring where the trail to Meadow Lake crosses Fordyce creek grains of a faintly greenish monoclinic pyroxene and probably also a little albite occur together with abundant quartz, tourmaline, epidote and pyrite. The occurrence of pyroxene in veins of this class is certainly not usual. Pyroxene is however not exclusively an igneous mineral; Daubrée has long ago shown that it may be formed by the action of superheated water on glass containing iron, and according to Brögger† it sometimes occurs in the veins of the syenite of southern Norway together with zeolites and calcite in such a way that it must be regarded as having been formed contemporaneously or even later than the zeolites.

<sup>\*</sup> Mr. Alfred R. Conkling, who for some time was engaged as a geologist of the Wheeler Survey, makes indeed the startling statement that "the ore deposits at Meadow Lake are generally found in a mass of basalt enclosed in the country rock, gray granite." Annual Report of Chief Engineer, 1878, Appendix NN, p. 183.

<sup>+</sup> Zeitschr. Kryst. u Min., xvi, p. 329.

#### 206 H. Gruener-Standard Solutions of Tartar Emetic.

From the data given above it appears probable that the larger part of contents of the veins should be regarded as country rock intensely altered by solutions containing heavy metals and boron, ascending along narrow cracks and fissures.

Somewhat similar deposits have recently been described by W. Moericke from Chile.\* In these occurrences a hornblendebiotite-granite of probably Tertiary age is in the vicinity of the veins altered to a tourmaline rock nearly identical with that here described; the veins proper occur in this tourmaline rock and consist of quartz with but little tourmaline, together with auriferous copper ores.

Washington, D. C., April, 1893.

#### ART. XXXI.—The Stability of Standard Solutions of Tartar Emetic; by HIPPOLYTE GRUENER.

[Contributions from the Kent Chemical Laboratory of Yale College—XXVI.]

DURING the progress of some investigations on antimony, I found it desirable to know to what extent a solution of tartar emetic could be relied on to retain its strength when kept for a length of time. Accordingly I made up a number of solutions of tartar emetic, whose strength was determined by titration in presence of an alkaline tartrate and bicarbonate with decinormal iodine, standardized against arsenious oxide. These solutions were put aside in stoppered bottles for a number of months, when they were again determined with iodine standardized against the same arsenious oxide.

Solution A was simply tartar emetic in distilled water, 16 grms. to the liter. At the end of five months this was found to have lost strength to a considerable extent, while a deposit, seemingly a mixture of antimonious oxide and of fungus growth had settled at the bottom of the bottle. At the end of fourteen months a still greater loss of strength was observed, corresponding in all to about 3.5 per cent of the tartar emetic, of which 4 grms. were present. The sediment was drained, dissolved in tartaric acid and titrated with iodine. It was found to correspond to '13 grm. of tartar emetic or approximately the amount lost. This shows clearly that under the conditions no great loss is caused by the formation of the pentoxide, in closed bottles at least.

Solution B was slightly alkaline with sodium bicarbonate in presence of sodium tartrate. On this solution after five months there was developed in addition to a fungus growth a

\* Min. und Petr. Mitth., xii, No. 3.

deposit, probably antimonious oxide; there was here a slight loss in the strength of the solution, amounting to 1 per cent.

Solution C was acid with tartaric acid only. After ten months the solution was found of the same strength and clearness as it was originally: but four months later there was a slight deposit accompanied by a loss of 1.2 per cent.

Parallel experiments to A gave like results. Two repetitions of C with varying amounts of tartaric acid present showed in each case a decided fungus growth with no loss of strength at the end of five months, whereas at the end of nine months the loss amounted to 1 per cent for the larger amount of tartaric acid and 0.3 per cent for the smaller amount.

It seems then that there is little danger of any oxidation of the antimonious oxide occurring, and provided enough tartaric acid is present to keep all the antimonious oxide in solution, the solution should maintain its strength for at least five or six months. The fungus growth has not been found to interfere in practical work with the solutions, yet it seemed advisable to prevent its formation if it could be done simply. To test the possibility of this, a number of solutions were prepared containing varying amounts of hydrochloric acid, which should act as a sterilizer; enough tartaric acid was added to counteract any tendency toward precipitation. In one series of experiments the solutions were sterilized at the beginning by boiling; in the other series distilled water which had been exposed more or less to the air for a number of days was directly used. Where the solutions had been thus sterilized no sign of fungus growth had appeared at the end of five months, and in the case of the unsterilized solutions there was never more than a trace. Where the hydrochloric acid present was not more than 10 cm<sup>3</sup> to 500 cm<sup>3</sup> of water, there was at the end of three months only the faintest trace of a deposit and no material loss of strength. Where the hydrochloric acid was present to the extent of 25 cm<sup>3</sup> in 500 cm<sup>3</sup> of water a decided granular precipitate was observed, accompanied by a loss of strength of about 10 per cent. The granular precipitate dissolved in tartaric acid and titrated accounted almost exactly for this loss.

A number of solutions were prepared under varying conditions and left open to the air for three months, at the end of which time no loss from oxidation was found.

It may be seen that tartar emetic in a solution of 16 grms. to the liter is not oxidized either in closed or open bottles. If it is desired to keep this solution as a standard for a moderate length of time it can be done in presence of enough tartaric acid (20 to 30 grms. to the liter) to prevent precipitation. The addition of  $1^{\text{cm}}$  hydrochloric acid to one liter of solution is enough to prevent any decided formation of fungus growth, at the same time not enough to cause a deposit as happens when large amounts of hydrochloric acid are used.

In the titration of tartar emetic in presence of starch the permanent blue color was taken in every case as the indication of the end reaction, as all other shades of color were found unsatisfactory. It is a well known fact that in the titration of antimony salts the color of the starch iodide is not developed until there is a considerable excess of iodine present, so that as compared with arsenious oxide, iodine gives high results with antimony. Thus, for example, the mean of six series of determinations made at various times and aggregating twentynine determinations showed the presence of 43.95 per cent of antimonious oxide in tartar emetic. (Sb = 120 and tartar emetic KSbOC, H, O,  $\frac{1}{2}$ H<sub>a</sub>O = 332, requiring 43.37 per cent.)

The facts above shown, that tartar emetic may be kept in stable solution by means of tartaric acid and hydrochloric acid in the proportions given, make it possible to use and keep such solutions for standardizing iodine for the determination of antimony, and thus to eliminate the error due to the tardy development of the starch iodide blue in presence of antimony salts, observed when compared arsenious oxide is used as a standard.

## ART. XXXII.—Description of Rowlandite; by W. E. HIDDEN and W. F. HILLEBRAND.

#### I. Historical and Descriptive Discussion, by W. E. Hidden.

ABOUT one kilogram of the mineral described in this paper was found by the writer in rather large lumps among huge masses of gadolinite and yttrialite, in a single shipment of the various yttria-bearing minerals, sent to him some five years ago, from the noted locality in Llano County, Texas.

The alteration products attracted my attention at once by their dissimilarity to those of gadolinite, yttrialite and allanite from the same mine. Several preliminary trials proved the mineral to contain over sixty-one per cent of the "rare earths" having a joint atomic weight of 118.5. The ignited oxalates had a pale straw color and the absorption spectrum of a saturated nitrate solution showed the lines of the erbium and didymium groups very prominent. Ferrous-oxide was found to be present (in one instance estimated at 4.69 per cent) and by the use of ammonium carbonate 0.40 per cent of what appeared to be uranium oxide was separated from the iron

### Hidden and Hillebrand—Description of Rowlandite. 209

solution. Three determinations of silica gave 25.98 per cent, 26.46 per cent and 25.64 per cent. A small amount of lime was also found. The loss on ignition was 2.01 per cent, but this was then considered as wholly due to hydroxyl and that fluorine was present was not even suspected. The apparent shortage, of nearly 5 per cent, was thought to be due to alkalies, magnesia and other non-essential elements and also to the fact of the hurried character of these preliminary analyses. That the mineral was essentially unlike gadolinite and could not be considered as a non-thoriferous yttrialite seemed proven and so it was laid aside until it could be looked into thoroughly.

Prof. Rowland photographed the spectrum of this mineral and also the "earths" from its oxalates and found them to be not essentially different from those of gadolinite and other minerals rich in yttria. He, however, expressed the opinion that there were at least *a dozen unknown elements* in the socalled yttria group not yet separated. The scale on which he showed its spectrum represented a length of ten feet and over *ten thousand* lines were noticed.

Later, the density was determined as 4.515, on carefully selected fragments. Its color varies from bottle- to pale drabgreen when pure and its luster on a fractured surface is decidedly more vitreous than that of gadolinite. It is also more transparent, being perfectly so, in thin splinters. Its alteration product is of a waxy-brick-red color tending towards brown and this is peculiarly characteristic. The alteration has been one of further oxidation of the iron, hydration and partial change to carbonates.

The mineral is isotropic, its hardness is 6, its fracture glassyconchoidal, its luster vitreous-resinous and the powdered mineral is light greenish gray. It is easily soluble in acids with gelatinization. Before the blowpipe it swells up without appreciable glowing but when strongly heated it emits a brilliant light without fusing. Any change of density was not investigated. The above data warranted me in calling the mineral new and quite distinct from gadolinite with which it is found associated. I proposed therefore, in a note published in this Journal in November, 1891, "the name of *Rowlandite* after Professor Henry A. Rowland, whose spectrographic work on the so-called 'rare earths' is so novel and important." Through the kindness of Prof. F. W. Clarke, of the U. S.

Through the kindness of Prof. F. W. Clarke, of the U. S. Geol. Survey, it has been possible to complete the description of this new mineral with the analysis and discussion of its composition by Dr. W. F. Hillebrand, given in the following pages.

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#### 210 Hidden and Hillebrand—Description of Rowlandite.

#### II. Analysis and Discussion of composition, by W. F. Hillebrand.

The specimen of rowlandite, furnished by Mr. Hidden for analysis, was a portion of a mass resembling somewhat amorphous gadolinite. It had a glassy interior surrounded by an uneven thickness of reddish alteration substance, chiefly a carbonate, or carbonates, of the rare earths and lime. The glassy "rowlandite" showed, when broken up, reddish and dark stains in places, the latter being produced by minute black inclusions, perhaps of a titanium mineral. Numerous scarcely visible fissures, filled with foreign matter, traversed the glass. This rendered the selection of pure material an arduous task; the result of several days of labor, however, was a sample possessing a high degree of purity as shown by the microscope. A very small amount of impurity was still present, but much less, apparently, than the analysis seems to indicate. A slight cloudiness in some grains points to incipient change. Its density is the same as that found by Mr. Hidden, 4.513, at  $15.5^{\circ}$  C. The analysis is as follows:

			Mean.		
SiO,	25.77	26.04	26.04*	k	
			•39		
ThO <sub>2</sub>	.59		•59		
Ce <sub>2</sub> O <sup>2</sup> ,‡	5.06		5.06		
La group	9.34		9.34	Mol. Wt. 336.8	
Yt group	47.70		47.70	Mol. Wt. 266.2	
Fe <sub>2</sub> O <sub>3</sub>	.09		•09		
FeÖ	4.39§		4.39		
MnO		•64	•67		
CaO	•60	•40	•50		
MgO	1.58	1.66	1.62		
Alk		•24	•28		
Н,О	•24		•24		
CÔ,			•34		
Fl			3.87		
P <sub>2</sub> O <sub>5</sub>	trace		trace		
			<u>.</u>		
			101.12		
	Less O for	r Fl,	1.63		
			00.40		

99.49

\* Certainly more nearly correct than 25.77, since the fluorine must have caused loss of silica on evaporation with hydrochloric acid.

+ A mixture of undefinable earths with some uranium and a trace of titanium.  $\pm$  Cerium dioxide cannot be present, if at all, in more than trivial amount, for otherwise much less ferrous oxide would have been found. For the same reason the manganese cannot be present as  $Mn_2O_3$ .

§ If the small and undetermined amount of uranium exists as dioxide, the ferrous oxide here given is correspondingly high, but the possible error can have no influence on the formula deduced. In calculating the molecular ratios a brief consideration shows that CaO and CO<sub>2</sub> may be neglected, and likewise, so far as their effect on the general formula is concerned, the ThO<sub>2</sub> and the group denominated X; also the trace of ferric oxide and the alkalies. For the present the water may also be disregarded. There result then the following molecular ratios :

SiO,	26.04 -	÷ 60 =	:	•4340	3.91
Ce <sub>2</sub> Õ <sub>3</sub>	5.06	328.4	.0154 )	h e ser e	
La group	9.34	336.8	.0277 }	· ·2223	2.00
Y group	47.70	266.2	(.1792)	1	
FeO	4.39	72	·0610)		
MnO	-67	71	.0094	· ·1109	1.00
MgO	1.62	40	.0405		
F1	3.87	19		2037	1.84

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

# Si43"R44"R11F20O154

The silica is in all probability as much as half a per cent too low through loss occasioned by the presence of fluorine. Furthermore, it is possible that the fluorine, estimated by the Berzelian method, is a little too low; or, if not, that the small amount of water found is in part at least derived from hydroxyl replacing fluorine. The presumption is then strong that the composition of rowlandite is represented by the formula

 $Si_{44}^{''}R_{44}^{''}R_{11}F_{22}O_{154}$ , or in simplified form  $Si_{4}^{'''}R_{4}^{''}RF_{2}O_{14}$ Structurally this formula may perhaps be written in a number of ways, that which most readily suggests itself being

$$\stackrel{'''\mathrm{RF}}{\underset{{}^{\prime\prime}\mathrm{Si}_{2}\mathrm{O}_{7}\equiv'''\mathrm{R}}{\overset{\parallel}{\underset{{}^{\prime\prime}\mathrm{Si}_{2}\mathrm{O}_{7}\equiv'''\mathrm{R}}}}}$$

in which the mineral is to be regarded as a derivative of the acid  $H_{e}Si_{2}O_{\tau}$ . Until, however, the whole group of rare earth silicates is carefully studied and their relations among themselves and to other better known silicates are ascertained, it would be premature to pronounce in favor of this or any other structural formula.

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

		Calculated for
]	ound.	$Si_4Y_4FeFl_2O_{14}$ .
Si	12.73	12.93
Y	50.83	50.37
Fe	6.50	6.46
Fl	4.05	4.39
0	25.89	25.85
1	00.00	100.00
	-	

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

### ART. XXXIII.—The Upper Hamilton and Portage Stages of Central and Eastern New York; by CHARLES S. PROSSER.

THE correlation of the Upper Devonian rocks of central and eastern New York has for a long time been a question of great difficulty and several interesting statements have recently been published in reference to this problem. The region is one familiar to me, and while recognizing the generally accurate description of the geologic sequence of this mass of rocks, the correlation and consequent age of a portion of the terranes under consideration, included between the base of the Oneonta sandstone and the top of the Hamilton stage, seem to call for a brief explanation of their paleontology and stratigraphy. This region was somewhat briefly described by Dr. H. S. Williams in a paper on "The classification of the Upper Devonian"\* in 1885; in addition to this a large amount of data has been accumulated in reference to the paleontology and stratigraphy of the region, the greater part of which is in the hands of Dr. Williams for use in the preparation of a monograph describing the Devonian system of the United States.

The term "Oneonta group" has been used for two entirely different geologic terranes in the same region of New York, hence it would seem advisable to review the history of the use of the names under consideration.

The Oneonta sandstone was defined by Vanuxem in 1840, as follows: "*Montrose sandstone*, or sandstone of Oneonta; this is the last or upper rock of the third district [third geological

\* Proc. Am. Assoc. Adv. Sci., vol. xxxiv, p. 225. See in particular Sections No. VIII, IX, X on the chart of meridional sections accompanying the paper.

district of New York]; it consists of many veins of gray sandstone, and sometimes of red sandstone . . . this rock is found in Otsego, Chenango and Broome counties [New York]; it covers the whole of the upper part of Susquehannah county, in Pennsylvania, and being there an abundant rock and surrounding the town of Montrose, I have thought it well to apply its name to this rock."\* This description classed as one formation the Oneonta sandstone, which in that region is overlaid by rocks containing at the base a Portage fauna, higher Chemung species and finally is capped by the Catskill stage, the united mass of these terranes forming Vanuxem's Montrose or Oneonta sandstone. In the same year, Professor Mather proposed the "Catskill Mountain series" and described it as "that [series] which lies between the Helderberg limestone series and the coal-bearing rocks of Carbondale in Pennsylvania."<sup>+</sup> In his following report Professor Mather subdivides this series into eight groups as follows :

"1. Conglomerates and grits.

(Red and gray grits with red shales mottled with green 2. spots.

- Montrose sandstone of Professor Vanuxem.
- Chemung group of Professor Vanuxem. 3.

4.	Ithaca "	"	"	"
5.	Sherburne flags	"	"	66
6.				
7.	Hamilton group	"	"	"
	Marcellus shales		"	·· ›› +

Vanuxem in his final report classed together the "Montrose and Oneonta Sandstone of the Reports" and called them the "Catskill group;" which he regarded as equivalent to the "Old Red sandstone of England."§

In 1841 Conrad published a classification of the rocks of The "formations" were numbered in ascending New York. scale and the following were referred by him to the "Upper Silurian Series":

- "26. Oneonta group.
  - 25. Cazenovia "
  - 24. Tully limestone.
  - 23. Sherburne group.
  - 22. Shales near Apulia.
  - 21. Black slate."

\*4th Ann. Rep. Third Geol. Dist. N. Y., p. 381.

+4th Ann. Rep. First Geol. Dist. N. Y., p. 227.

- t 5th Ann. Rep. First Geol. Dist. N. Y., p. 77. § Geol. N. Y., Pt III, 1842, p. 186.

5th Ann. Rep. Palæontology N. Y., p. 31.

There is one mistake in reference to the stratigraphic order of the groups of the above list. The "Cazenovia group" belongs *below* instead of above the Tully limestone. This error was corrected by Vanuxem in his final report, where under the heading of the Hamilton, the "Cazenovia group" is given as one of its divisions.\*

To one who is not familiar with the geological outcrops near Cazenovia, a glance at the geological map of New York of 1843, or the one showing the "Geographical distribution of the Tully limestone in central New York" by Professor S. G. Williams, + will show the exposures of Tully limestone as considerably south of Cazenovia. Of course the "Black slate" represents the Marcellus shale, while the "shales near Apulia," and the "Sherburne group" are parts of the Hamilton stage as stated by Vanuxem.<sup>+</sup> It is interesting to note that the term "Sherburne group" of Conrad is not the same as the "Sherburne flagstone and shale" of Vanuxem as will be seen from an attentive examination of his final report.§ The Sherburne flagstones of Vanuxem are a mass of sandstones in the Chenango Valley above the horizon of the Tully limestone, which are mostly non-fossiliferous and are synchronous with the lower part of the Portage as exposed farther west. Below these flagstones are argillaceous shales which contain an abundance of Hamilton fossils, as for instance in the shales at Rexford or Sherburne falls. The same zone is well exposed in the gorges near Smyrna where the Sherburne flagstones form the top of the high hills, and most of the species which Conrad gave as belonging to the "Sherburne group" were from "near Smyrna." The following, which are now all well known Hamilton species, were named and described :

Nuculites oblongatus, N. rostellatus, N. bellistriatus [now Nucula bellistriata], Orthonota undulata, Cypricardites oblonga [now regarded as a synonym of Modiomorpha concentrica (Con.) Hall], and C. rugosa [now Goniophora rugosa (Con.) Miller].

Above this zone Conrad placed the Tully limestone, but apparently no representative of the Genesee shale is given. The highest rocks are the Oneonta group which are supposed to have been named from exposures near that town. Nuculites cuneiformis, N. maxima [now Palconeilo maxima (Con.) Hall], and Cypricardites carinata [now Goniophora carinata (Con.) Hall] were named and described from this formation at

<sup>\*</sup> Geol. N. Y., Pt. III, p. 150.

<sup>+</sup> Sixth Ann. Rep. State Geologist [N. Y.] for 1886; map following p. 28.

<sup>‡</sup> Geol. N. Y., Pt. III, p. 150.

See the explanation of the names that had been used for different parts of the Hamilton on p. 150, and the same for the Portage on p. 172.

<sup>5</sup>th Ann. Rep. Palæontology N. Y., pp. 50-54.

The shales and sandstones which contain these Oneonta. fossils are exposed at the base of the high hill near Oneonta. and are below the reds and grays which compose the terrane to which Vanuxem gave the name Oneonta sandstone. The quarry, a short distance west of Oneonta and below the highway, contains these species in association with others, especially Paracyclas lirata (Con.) Hall, Chonetes scitula Hall and Tropidoleptus carinatus (Con.) Hall. Above the highway fossils become rare and gradually disappear, the last species noted being Nuculites cuneiformis Con. and Palconeilo maxima (Con.) Hall, about half way up the hill. It seems that Conrad's name for this zone was not considered in the final reports of the New York Survey, although Vanuxem referred to the horizon in several places; for instance in describing the hill near Oneonta, mentioned above, it is stated that the Catskill group or Oneonta sandstones of Vanuxem "occupy the highest part of the face of the hill, the base of which is composed of rocks which I [Vanuxem] have supposed to belong to the Ithaca group." \*

So far as the writer is aware he first called attention to the twofold use of the term "Oneonta group," and indicated the stratigraphic place of each zone. † The zone is well exposed in the Susquehanna, Unadilla, and Chenango river valleys, especially at Oneonta, Oxford and Norwich. In reference to the correlation of the deposits below the Oneonta sandstone there seem to be many conflicting opinions, owing to the fact of the absence of the Tully limestone and the Genesee shales in central and eastern New York. It is true that their distinctive lithologic characters simplify the matter of separating the Hamilton from the overlying Portage in all that area where they are present. But the writer found that a careful study of the facies of the fauna of each zone, supplemented by actual observation of their stratigraphic position and relation in the field, enabled him to separate the fauna of the typical Hamilton from those of the modified Hamilton faunas of the overlying rocks in regions where there was no trace of the Tully limestone or Genesee shale.

This method of separating the Hamilton from the Portage above was thoroughly tested during the summers of 1890–91 in an examination of the Devonian system along the eastern face of the Catskill mountains from Greene county, New York, to Carbon county in eastern Pennsylvania. It was noted that although the fossils in the upper rocks were mostly species found in the typical Hamilton of central and western New York, still there were slight variations or even varietal modifi-

\* Geol. N. Y., Pt. III, p. 192.

+ Proc. Am. Assoc. Adv. Sci., vol. xxxvi, 1887, p. 210.

cations which when observed, enabled one to separate them. There are frequently lithologic variations to assist, as in eastern Pennsylvania, which were used to advantage in the work of Prof. I. C. White for the 2d Geological Survey of that State, and a knowledge of these *two* characters was found necessary for the correlation of the Upper Devonian of this region. This principle was tested several times by different observers and it was found that those paleontologists who had simply studied the species in a general way without considering the minor variations due to the difference in geographic distribution or stratigraphic range did not recognize the different facies of these faunas but called them all Hamilton; while two paleontologists who had closely studied the characters of the faunas and had also noted similar comparatively slight changes in reference to the distribution and range of species for another region, on being shown collections of these fossils without any information as to their stratigraphic position, invariably recognized those that came from the beds corresponding to the typical Hamilton of New York, as well as the slightly modified faunas from the overlying rocks. And this recalls the principle stated by Dr. H. S. Williams when describing the classification of the Upper Devonian for southern and western New York, viz:-""the complications arising from both geological and geographical modifications of fossil faunas are so great that the attempt to determine horizons by single or by roughly identified fossils will certainly lead to erroneous results."\* The failure on the part of paleontologists to observe this rule and the tendency on the part of the stratigraphic geologists to base their correlations mainly on lithologic characters have continually made futile all attempts toward an accurate correlation of the terranes of the Upper Devonian for southern and eastern New York, and eastern Pennsylvania.

In a recent article is the statement that "the basal bcds [of the Oneonta formation | are gray flags which merge into the Hamilton ;"+ but no data is given in favor of such correlation and I suppose the opinions of other geologists were followed.

This particular part of the series is one to which the writer of this paper has given especial attention, not only so far as the fossils from the different regions and horizons are concerned but he has also made cross sections at various points from

\* Proc. Am Assoc. Adv. Sci, vol. xxxiv, 1886, p. 231.

<sup>†</sup>The stratigraphical relations of the Oneonta and Chemung formations in eastern Central New York; by N. H. Darton. This Journal, III, vol. xlv, p. 206. In addition see on p. 207 the statement that the Hamilton is exposed at Lyon Creek bridge, near Oxford; also, that "The Chemung rocks to which Mather and others refer lies below the Oneonta beds or about 1,000 feet below the actual base of the Chemung horizon, and are Hamilton in position. This fauna is meagre and consists of species supposed by Vanuxem to be Chemung in central New York, but now known to be Hamilton

central New York to central Pennsylvania and traced the continuation of the different zones, so that he feels inclined to speak with considerable positiveness in reference to this portion of the New York Upper Devonian. Moreover, since a new geologic map of New York is in process of coloration, it seems that attention should be called to the correlation of this particular part of the series. Indeed, most of the statements that have been made during the last ten years as to the age of these rocks are not so accurate as the conclusions of Vanuxem over fifty vears ago; so that if this area be colored on the new map, as one would infer from these occasional statements, the map for that section of the State will not be so accurate as the one of 1843. These remarks apply especially to that part of the geologic column which in western central New York extends from the Genesee shale to the base of the Chemung, while for central and eastern New York and Pennsylvania from the Marcellus shale to above the lower reds and grays, called the Oneonta sandstone, as high as marine fossils have been found.

Our reason for differing from the ordinary statements in reference to the age of the rocks immediately underlying the Oneonta sandstones (which compose the Oneonta group of Conrad) will be much more clearly understood if we consider first a section like that of Cayuga lake, where the Tully limestone and Genesee shale are present in their full development, and consequently where there can be no question as to the upper limit of the Hamilton stage as originally defined and generally understood and accepted. The bluffs along Cayuga lake and the exposures south of Ithaca, which have been carefully studied and fully described by Dr. H. S. Williams in various publications, afford such a section.\* Along the shores of Cayuga lake are exposed 1,000 feet of argillaceous shales and sandstones containing an abundant and typical Hamilton fauna. Capping the Hamilton is the Tully limestone varying from 15 to rather more than 20 feet in thickness. This is overlaid by the Genesee shale, a very fissile, black, argillaceous shale 100 feet in thickness in this region which in some of the glens, as Burdick's, is capped by a prominent sandstone nearly four feet in thickness. The sandstone marks the beginning of the Portage, the lower division of which is composed of sandstone and shales containing but few fossils with a thickness of 250 feet. Succeeding this division is the "Ithaca group" of Vanuxem, or the middle Portage of Professor Williams, with a thickness of

<sup>\*</sup>See particularly Bull. U. S. Geol. Survey, No 3, 1884; also Science, vol. i, old series, Oct. 16, 1880, p. 190, Proc. Am. Assoc. Adv. Sci., vol. xxx, p. 1, of reprint, and ibid, vol. xxxiv, p. 222.

<sup>This part constitutes the entire Portage of the Cayuga lake region as described by Professors Hall and Vanuxem in their final reports. See Geol. N. Y., Pt. IV, p. 250, and ibid., Pt. III, p. 174.</sup> 

450 feet. Portions of this division contain abundant fossils and the fauna is made up of an assemblage of Hamilton, Portage of western New York and a few species which are found in the Chemung, together with those that are peculiar to the Ithaca zone. Following the "Ithaca group" are 600\* feet of shales containing only a few fossils which are mainly the same as those of the Lower Portage. Professor Williams, who first noticed and described this zone, called it the Upper Portage and consequently assigned to the entire Portage of the Cayuga lake region, a thickness of 1300 feet. Succeeding these barren shales and sandstones are shales of different lithologic character which contain the regular Chemung fauna as known somewhat farther south in the typical locality near Chemung, and possibly row with better exposures near Waverly. In this section there has never been any question as to the upper limit of the Hamilton, and no one has proposed to call the rocks of the "Ithaca group" with a modified Hamilton fauna, a part of the Hamilton stage. The Ithaca fauna was correlated differently by Vanuxem who called it "a group between the Portage and Chemung," and by Professor Hall who considers it the lower part of the Chemung stage; but both of these geologists overlooked the non-fossiliferous zone above, which was observed by Professor Williams, who has classified the rocks of this section in a perfectly satisfactory manner.

Now if we consider the section of central New York along the Chenango valley, we shall find a decided change in the order of the stratigraphic character of the section, although certain zones or stages may be and have been traced continuously by several geologists from Cayuga lake into the Chenango valley. The Tully limestone and Genesee shale are two stages which have been followed to a locality near Smyrna village in the northern part of Chenango county. To be sure they are much less in thickness than where exposed on Cayuga lake, still there is no question that they represent the same geologic horizon, as has been attested by every observer who has gone over this field. It was so understood by Vanuxem, in 1842;† more definitely described by Prosser in 1887;‡ the Tully limestone mapped with this eastern exten-

\*For the thickness of these divisions of the Portage see Prosser in Trans. Am. Inst. Min. Eng., vol xvi, p. 945; also for the thickness of the Upper Portage see this Journal, III, vol. xxxii, p. 193, where Professor Williams says: "The fossiliferous zone at Ithaca is separated from the lowest beds containing characteristic Chemung fossils by about 600 feet of nearly barren, flaggy and shaly deposits, but with a few fossils which belong to the characteristic Portage fauna."  $\dagger$  Geol. N. Y., Pt. III, pp. 164, 169 and 292.

<sup>‡</sup> Proc. Am. Assoc. Adv. Sci., vol. xxxvi, p. 210, where the thickness of the Genesee shale is given as 20 feet, and the limestone layers and calcareous shales as 25 feet, near Upperville in Smyrna township. sion by Professor S. G. Williams in the same year,\* and finally so indicated by Dr. H. S. Williams in 1890.+

The bearing of this horizon will be immediately appreciated when we remember that Smyrna is in the Chenango river valley, while Oxford is nineteen miles farther south in the same valley near which place it is stated the Hamilton is exposed. The fossiliferous zone near Oxford is well exposed at Norwich and on the hills near North Norwich, but farther north at Sherburne it is found only near the top of the high hills and at Smyrna it is hardly reached at the summit of the highest hills. Some of the species belong in the Portage and many occur in the Hamilton, among which are those slightly modified from the Hamilton forms. The recurrence of the Hamilton species in the higher beds has probably led several geologists to refer these rocks to the Hamilton stage, and to ignore the clear and perfectly conclusive stratigraphic evidence of their age. The most authoritative correlations of this zone with the upper part of the Hamilton stage are indicated in the following foot note.<sup>±</sup>

The stratigraphic sequence and general correlation of the Hamilton and Portage stages for Chenango and Otsego coun-ties were described by the writer in 1887;§ but at this time it

\* Sixth An. Rep. State Geol. [N. Y.] for 1886, p. 13; and see map facing p. 28.

† Bull. Geol. Soc. Am., vol. i, p. 489. † In the Geol. Surv. N. Y., Palæontology: vol. v, Pt. I, Lamellibranchiata II, 1885, several species are reported from localities in this zone which is called Hamilton; as Goniophora carinata (Con.) Hall, from Oneonta, p. 302; Microdom (Cypricardella) complanatus Hall, below Norwich, p. 312; Nuculites cuneiformis Con., at Oneonta, p. 326; Palæoneilo arata Hall, "shales of the Hamilton group, near Norwich," p. 342; Prothyris planulata Hall, near Norwich, p. 460; P. lanceolata Hall. Norwich, p. 461; Phthonia nodicostata Hall, near Oneonta, p. 474; and finally on p. 517 is the statement that the Oneonta sand-state state. stone "comes in at about the close of the Hamilton period, or more properly may be regarded as the result of changes which terminated the conditions of the Hamilton group," while on p. 518 the Upper Devonian of Otsego, Delaware, and Chenango counties is correlated as follows:

"Catskill group.

Chemung

Oneonta { Portage group. Hamilton (Upper).

Hamilton group."

A similar statement in reference to the age of these rocks occurs in *ibid*. Lamellıbranchiata I, as Leptodesma Rogersi Hall is reported "in the shales of the Hamilton group at Norwich, Chenango county," p. 177. Finally, in 1886, Professor Hall made the following statement in reference to a section near Oxford: "The results of the most recent investigations have served to substantiate my previous published statements, and clearly show that the Oneonta sandstone rests upon well marked Hamilton strata, and is succeeded by strata carrying the fossils of the Chemung Group " (Fifth An. Rep. State Geologist [New York] for 1885, p. 4). Also the section on p. 11 represents the lowest shales and sandstones as belonging to the "Hamilton group," and mentions Spirifera mesastrialis, Para-cyclas lirata, and Polæoneilo muta from these beds.

§ The paper was read at the New York meeting of the Am. Assoc. Adv. Sci., and an abstract published in vol. xxxvi, p. 210.

seems important to indicate more of the data upon which this classification was based. The upper zone of the Hamilton stage as exposed in the creeks and railroad cuts near Earlville, Smyrna and Sherburne, which was called the "Sherburne group" by Conrad, is composed of moderately coarse arenaceous shales which alternate with more argillaceous and calcareous shales containing abundant fossils. Along Pleasant brook above and below the Ontario and Western railroad station, in the edge of Smyrna village, as well as farther up the brook toward Upperville, are excellent exposures of these shales. Various species are abundant and careful search would be rewarded by a large list of Hamilton fossils. A moderate search has afforded the writer the following species from along Pleasant brook and other exposures near Smyrna village, Chenango county.

1.	Ambocælia umbonata (Con.) Hall	34.	Goniophora hamiltonensis Hall(rr)
	( <i>aa</i> )*	35.	Goniophora rugosa (Con.) Hall(rr)
2.	Spirifera fimbriata (Con.) Hall (cc)		$Grammysia \ arcuata \ (Con.) \ Hall(r)$
3.	Tropidoleptus carinatus (Con.) Hall	37.	Modiomorpha subalata (Con.) Hall
	<i>Chonetes coronuta</i> (Con.) Hall( <i>cc</i> )		( <i>rr</i> )
4.	Chonetes coronata (Con.) Hall(cc)	38.	Leptodesma Rogersi Hall (?)(rr)
5.	Chonetes deflecta Hall $(?)$ $(r)$	39.	Pterinopecten Vertumnus Hall(c)
6.	Chonetes setigera Hall(c)	40.	Cypricardinia indenta (Con.) Hall (r)
7.	Spirifera mucronata (Con.) Bill. (c)	41.	Modiella pygmæa (Con.) Hall(rr)
8.	Spirifera medialis Hall(rr)	42.	Microdon (Cypricardella) bellistriatus
9.	Spirifera granulifera Hall(a)		(Con.) Hall $(rr)$
10.	A trypa reticularis (Linn.) Dal $\dots$ (r)	43.	Grammysia constricta Hall(rr)
11.	Athyris spiriferoides (Eaton) Hall (rr)	44.	Nucula lirata (Con.) Hall(rr)
12.	Orthis Vanuxemi Hall	45.	Orthonota carinata Con(rr)
	Strophodonta perplana(Con.) Hall (rr)	46.	Leda rostellata (Con.) Hall(rr)
	Streptorhynchus chemungensis (Con.)		Palæoneilo muta Hall(rr)
	Hall $(r)$	48.	Phthonia cylindrica Hall(rr)
15.	Cyrtina hamiltonensis Hall(rr)	49.	Mytilarca (Plethomytilus) oviformis
16.	Cryptonella planirostra Hall(rr)		(Con.) Hall $(r)$
17.	Chonetes scitula Hall(c)	50.	(Con.) Hall(r) Tellinopsis subemarginata (Con.) Hall
18.	Cimitaria recurva (Con.) Hall(rr)		(rr)
19.	Paracyclas tenuis Hall(rr)	51.	Pterinea flabella (Con ) Hall(rr)
	Palæoneilo emarginata (Con.) Hall (r)		Cimitaria elongata (Con.) Hall_(rr)
	Schizodus appressus (Con.) Hall(rr)	53.	Phthonia sectifrous (Con.) Hall_(rr)
	Palæoneilo constricta (Con.) Hall_(rr)		Glytodesma erectum (Con.) Hall.(rr)
	Nuculites triqueter Con(c)	55.	Nucula corbuliformis Hall(rr)
	Nuculites oblongatus Con(rr)		Phacops rana (Green) Hall(c)
	Pholadella radiata (Con.) Hall(r)		Dalmanites Boothi (Green) Hall_(rr)
	Orthonota (?) parvula Hall(rr)	58.	Homalonotus DeKayi (Green) Em-
	Prothyris lanceolata Hall(rr)		mons
	Macrodon hamiltoniæ Hall(r)	59.	Platyceras carinatum Hall(rr)
	Leda diversa Hall	60.	Pleurotomaria capillaria Con. $\dots$ (r)
30.	Nucula bellastriata (Con.) Hall(rr)	61.	Coleolus tenuicinctum Hall(rr)
	Microdon (Cypricardella) tenuistria-	62.	Bellerophon crenistria Hall(rr)
	tus Hall	63.	Bellerophon Leda Hall
32.	Modiomorpha concentrica (Con.) Hall		Nucleospira concinna Hall(rr)
	(rr)		Chonetes mucronata Hall(rr)
33.	Modiomorpha mytiloides (Con.) Hall		Leiorhynchus multicosta Hall (rr)
	(r)		
÷	The relative abundance of the spec	cies	is indicated as follows:— $aa = very$

\* The relative abundance of the species is indicated as follows: -aa = very abundant, a = abundant, cc = very common, c = common, rr = very rare, r = rare.

On the upper part of Pleasant brook between five and six miles from Smyrna village is an exposure of Tully limestone which is probably the one mentioned by Vanuxem.<sup>\*</sup> The exposure is by the side of the brook, just above the highway bridge, where 26 inches of limestone are exposed with a blue argillaceous shale below, which contains plenty of fossils. The following species were obtained from this shale :—

	Spirifera mucronata (Con.) Bill(a)		
	Vitulina pustulosa Hall(a)		
3.	Tropidoleptus carinatus (Con.) Hall	7.	Palceoneilo emarginata (Con.) Hall
	(r)		( <i>rr</i> )
4.	Modiella pygmæa (Con.) Hall(rr)		

About one-half mile farther up the brook is an exposure of black, argillaceous, fissile shale, fifteen feet in thickness, in which an excavation has been made in search of coal. No fossils were found in the black shales, which are succeeded by rather thin sandstones.

There is a moderately steep hill west of Smyrna village and Pleasant brook, which is mostly covered above the gorge, though there are occasional exposures. In the highway near the top of the hill, in a small run, are smooth blue shales which are non-fossiliferous. In the field near the summit of the hill, about one mile west of Smyrna and from 475'-500' above the R. R., is a small excavation that was made in searching for flagging stones. The rock is a coarse arenaceous shale, not as blue as the lower exposure, and contains a few fossils.

The following species were obtained :

1.	Spirifera mesacostalis Hall(c)	6.	Atrypa reticularis (Lin.) Dalman (rr)
2.	Spirifera fimbriata (Con.) Bill.(?) (r)	7.	Chonetes setigera Hall(rr)
3.	Cyrtina hamiltonensis Hall(c)	8.	Ambocælia umbonata (Con.) Hall
1.	Leiorhynchus mesocostalis Hall (c)		(r)
5.	Productella cf. speciosa Hall $\dots(r)$	9.	Phacops rana (Green) Hall(rr)

Below Upperville a small run, on the western side of Pleasant brook, gives a section from the fossiliferous Hamilton shales up through the Tully limestone and Genesee black shales into the overlying barren Portage. The shales in the lower part of the run contain specimens of

\*See Geol. N. Y., Pt. III, 1842, p. 164, where Vanuxem says under "localities where observed.—The first point going west is on the turnpike from Sherburne to DeRuyter, about eight miles from the former village." Also under the geological description of Chenango county it is stated:—"The *Tully* limestone was seen but in one locality at the north western part of Smyrna, on the road to DeRuyter village where the road crosses the west branch of the Chenango," *ibid.*, p. 292. This outcrop was considered by Prof. S. G. Williams as the one described by Vanuxem (Sixth An. Rep. State Geologist [N. Y.], 1886, p. 18).

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Above this zone about twenty-five feet of rather sandy limestone alternating with shales are exposed, and above the limestone twenty feet of black, fissile shale in which no fossils were found. Overlying the black shale are thin, regular sandstone layers, one-fourth to one-half inch thick which at first alternate with blocky, blackish argillaceous shales. The sandstones gradually become thicker for some distance and then are overlaid by blue, smooth shales which weather to an olive color. Beyond Upperville, twenty-five feet above the highway along which the black shales are exposed, a small quarry has been opened in the sandstone in which an occasional fossil occurs. Some search revealed only the following forms :—

1. Lunulicardium fragile Hall ... (rr) 3. Crinoid stems.

2. Leiopteria —— sp.....(rr) Leiorhynchus mesocostalis Hall (rr)

A single specimen of the last species was found, which was not surely in place in the quarry, but possibly came from higher up the hillside.

The section on the upper part of Pleasant brook and the one just described on the hillside below Upperville, taken in connection with the one up the hill west of Smyrna show a passage from blue, argillaceous shales containing an abundant Hamilton fauna, up through the impure Tully limestone, the black Genesee shale, a sandstone zone and another of blue shale into coarse arenaceous shales or thin sandstones containing a meagre fauna, the species of which are found in the Portage and Ithaca groups. It seems to me there is no question but that the section passes from the Moscow shale of the upper Hamilton through the Tully limestone and Genesee shale into the lower Portage.

At Sherburne there are not such clear sections of the transition deposits from the Hamilton to the Portage, as at Smyrna; but there are excellent exposures of the upper Hamilton as well as some of the moderately fossiliferous overlying Portage.

Along Mad brook east from Sherburne village for one mile to Harrisville, rising from about the R. R. level to an elevation of 240' above, at the reservoir in Harrisville, are numerous and excellent exposures of blue argillaceous shales with some coarse blue arenaceous shales forming the upper portion of the Hamilton stage. A limited search in the shales along Mad brook yielded the following species:—

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1.	Chonetes coronata (Con.) Hall_(aa)	26.	Macrodon hamiltonice Hall(rr)
2.	Chonetes setigera Hall(aa)	27.	Modiella pygmæa (Con.) Hall( $c$ )
3.	Chonetes lepida Hall(rr)		Orthonota (?) parrula Hall(r)
4.	Spirifera mucronata (Con.) Bill.(aa)	29.	Orthonota carinata Con(r)
5.	Spirifera granulifera Hall(rr)	30.	Orthonota undulata Con( $\dot{r}$ )
	Spirifera fimbriata (Con.) Hall (rr)	31.	Cimitaria elongata (Cen.) Hall_ $(r)$
7.	Ambocælia umbonata (Con.) $Hall(r)$	32.	Pholadella radiata (Con.) Hall (aa)
8.	Athyris spiriferoides (Eaton) Hall	33.	Prothyris lanceolata Hall (rr)
	(r) Orthis Vanuxemi Hall(r)	34.	Grammysia arcuata (Con.) Hall (c)
9.	Orthis Vanuxemi Hall(r)	35.	Modiomorpha mytiloides (Con.) Hall
10.	Strophodonta perplana (Con.) Hall		( <i>rr</i> )
	(r)	36.	Sphenotus solenoides Hall(rr)
11.	Strophodonta inequistriata (Con.)		Tellinopsis subemarginata (Con.)
	Hall(a)		Hall(rr)
12.	Streptorhynchus chemungensis	38.	Cypricardinia indenta (Con.) Hall
	(Con.) Hall $(r)$		( <i>rr</i> )
13.	Tropidoleptus carinatus (Con.)Hall	39.	(rr) Microdon (Cypricardella) bellistri-
	(c)		atus (Con.) Hall(rr)
14.	Spirifera tullia Hall(rr)	40.	Glyptocardia speciosa Hall(rr)
	Chonetes mucronata Hall(rr)	41.	Goniophora hamiltonensis $Hall_{(r)}$
16.	Chonetes scitula Hall(rr)	42.	Mytilarca (Plethomytilus) ovifor-
17.	Nuculites triqueter Con(aa)		mis (Con.) Hall( $r$ )
18.	Nuculites oblongatus Con. $\dots$ (r)		$Loxonema \ delphicola \ Hall \dots(a)$
19.	Pal coneilo constricta (Con.) Hall(a)	44.	Pleurotomaria capillaria $Con(r)$
20.	Palœoneilo emarginata (Con.) Hall		Bellerophon Leda Hall $\dots$ (r)
	( <i>r</i> )	46.	Bellerophon acutilira Hall(rr)
	Palceoneilo muta Hall(r)	47.	Coleolus tenuicinctum Hall $\dots(r)$
22.	Nucula bellistriata (Con.) Hall(c)		Dalmanites Boothi (Green) Hall (c)
23.	Nucula corbuliformis $Hall_{\dots}(r)$	49.	Phacops rana (Green) Hall(r)
24.	Nucula lirata (Con.) Hall( $r$ )	50.	Homalonotus De Kayi (Green) Em-
25.	Paracyclas tenuis Hall(rr)		mons $\dots$ $(rr)$

About one mile southeast of Sherburne village is a high hill near the foot of which, about seventy-five feet above the R. R. level or 1117' A. T.,\* are somewhat coarse arenaceous shales with a moderate number of fossils, principally of the large species, as *Spirifera granulifera* Hall and its usual associated species. The fauna is distinctively Hamilton and the shales are in the Hamilton stage. Then for a distance of 440' the hill slope is covered and at an elevation of 515' above R. R. level or 1557' A. T., there is an outcrop of coarse arenaceous shales alternating with thin blue flagstones. This bed contains some fossils and the fauna is the same as that of the highest exposures on the hills near Smyrna. The blue argillaceous shale, black shale and limestone below this zone are not shown in this section, on account of the thick deposit of drift.

About three miles north of Sherburne is the Mulligan quarry, at the top of a high hill, which furnishes thin blue flagstones with coarse irregular shales above them, containing fossils similar to those near the top of the hill west of Smyrna and the one southeast of Sherburne. By the barometer, this exposure is from 424' to 446' above the R. R., or 1466' to 1488' A. T.

\* The R. R. station at Sherburne is 1042' A. T.

At North Norwich, five miles south of Sherburne the zone of blue argillaceous shales, with no fossils, is well exposed along Blue or Cold brook, about 76' above R. R. level or approximately 1099' A. T.\* At about 144' above R. R. or approximately 1167' A. T., is the base of the zone containing fossils. This zone is well exposed in the old Harris, now known as the Wilkes, quarry which was mentioned by Van-uxem<sup>+</sup> and is in the edge of Plymouth, about 305' above R. R. level or approximately 1378' A. T. Exposures near the top of the hill 427' above the R. R. or approximately 1456' A. T., still contain the same fauna.

In the Harris or Wilkes quarry the following species were found:

- 2. Atrypa reticularis (Linné) Dal. (cc)
- 3. Leiorhynchus mesocostalis Hall (c)
- 4. Chonetes scitula Hall (?) \_\_\_\_\_(a)

This species is abundant; but in the condition of impressions renders identification difficult. Some of the specimens approach C. setigera Hall in form, though they are not so convex near the umbo as those found at Ithaca.

- 5. Chonetes lepida Hall .....(rr)
- 6. Cyrtina hamiltonensis Hall ...(rr)
- 7. Strophodonta sp. \_\_\_\_, \_\_\_\_(rr)

Two imperfect impressions which are similar to S. perplana (Con.) Hall.

ata (Con.) Hall or M. tenuistri-

ata Hall .....(rr)

A single specimen which has the proportions of M. bellistriata as well as those of the elongated form of M. tenuistriata Hall (see Pl. 73, fig. 28). It is impossible to determine whether the specimen has the fine striae of M. tenuistriata or the coarse striae of M. bellistriata.

10. Paracyclas lirata (Con.) Hall\_.(rr) 11. Cimitaria recurva (Con.) Hall\_(r) 12. Palæoneilo emarginata (Con.) Hall (*rr*)

1. Spirifera mesacostali: Hall.....(c) | 13. Goniophora carinata (Con.) Hall (?) .....(*r*)

This species is reported from Copley's quarry at Oneonta. ‡ A comparison of specimens from the two localities fails to prove them precisely similar; but the North Norwich specimens are nearer this species than any of the others figured in this work.

14. Modiomorpha sp. (a broken specimen) ......(rr)

15. (?) Glossites depressus Hall ....(rr)

A single specimen which apparently belongs to this genus and species.

16. Palceoneilo constricta (Con.) Hall 18. Leptodesma cf. Rogersi Hall ... (r)

These specimens do not have as mucronate ears as most of those figured; but some of them resemble closely the one figured on pl. 21, fig. 9 (Pal. N. Y., vol. v, Pt. I, Lamell. I), which is stated to be from the Hamilton shales at Norwich, N. Y.

19. Streptorhynchus chemungensis (Con.) Hall..... . **\_ \_ \_**(r)

20. Actinopteria Boydi (Con.) Hall (rr) 21. Phacops rana (Green) Hall .... (rr)

Of the seventeen species specifically identified in the above list, counting those that are questioned, there are twelve that occur in the "Ithaca group" at Ithaca. The general range of the other five species is as follows:

\* The R. R. station at North Norwich is about 1023' A. T.

\* See Geol. N. Y., Pt. III, 1842, pp. 178, 293.
\* Pal. N. Y., vol. v, Pt. I, Lamell. II, p. 302; see pl. 44, fig. 7 for figure of form similar to the North Norwich specimen.

Paracyclas lirata (Con.) Hall, common in the Hamilton of central and eastern New York, and then extends well up into the Portage; Cimitaria recurva (Con.) Hall, Hamilton of central New York and reported from Mt. Upton\* which is near the same horizon as the Norwich and Oneonta zone; Goniophora carinata (Con.) Hall, from Oneonta and Mt. Upton and consequently in this zone; Leptodesma Rogersi Hall, in the upper Hamilton and at Norwich; † and Phacops rana (Green) Hall, is reported doubtfully from the Upper Helderberg and occurs in the Marcellus, Hamilton, Tully limestone, and Chemung. Consequently it is clear that so far as the fossils are concerned this list show, a closer relationship with the "Ithaca group," as stated by Varuxem in 1842,‡ than with any other stage. To be sure most of the species occur in the Hamilton stage, but so do the majority of the species found in the "Ithaca group" at Ithaca, and judged by that alone the zone might be referred to the Hamilton instead of the Portage where its stratigraphical position and other evidence show it to belong.

At Norwich, six miles south of North Norwich, the base of this zone has been carried by the dip below the surface. A number of observations along the Chenango valley indicate the dip to be between 35 and 40 feet per mile for that region. The high hill west of Norwich affords a good section of 550 feet. At the base of the hill on the Canaswacta creek are the lowest rocks, at an approximate elevation of 985', which are bluish rather arenaceous shales containing fossils. At 1140' is the base of an old quarry which runs up to 1193' and in this quite a good many fossils were found. The most common species are Paracyclas lirata Con., Chonetes scitula Hall, Tropidoleptus carinatus Con., Rhynchonella Stephani Hall (?) and Atrypa reticularis (Linné) Dal. At 1230' are the last shales containing fossils below the reds and grays. The most abundant fossils are segments of crinoid stems, but with these are specimens of *Paracyclas lirata* Con. and *Cypricardella* (Microdon) bellistriata (Con.) Hall. At 1262' are rather fine fissile shales which are succeeded by coarse sandstones at 1370'. A prominent concretionary sandstone occurs at 1410' and at 1460' is a coarse gray sandstone. The first red shale resting on thin fissile olive shales, occurs at 1475' and in the red shales at about 1479' is a somewhat calcareous layer with pebbles containing numerous fish scales which are found to a less extent in the red shales close to this stratum. The red shale stops

\* Pal. N. Y., vol. v, Pt. I, Lamell. II, p. 468.

*Ibid.*, Lamell. I, p. 177. See Geol. N. Y., Pt. III, p. 178, where this quarry is described under the head of the Ithaca group.

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near the altitude of 1500' and is succeeded by coarse gray sandstone which continues to the top of the hill with an approximate altitude of 1555'. At 1535' is Crandall's flagstone quarry in coarse gray sandstone. In a cut on the D. L. & W. R. R. less than one-half mile north of the station, and in the quarries along Ransford creek, toward the reservoir northeast of the village, are excellent places for collecting fossils.

In a small creek about one mile north of Oxford or seven miles southwest of Norwich are exposures of shale containing the same fauna as at Norwich, though this is near the upper part of the zone which soon disappears beneath the surface. On the eastern side of the Chenango valley, at the Lyon Brook Bridge of the O. & W. R. R. is a good section showing the top of the Oneonta zone in the creek below the bridge with the lowest red shales about 150 feet higher, in an old quarry just east of the south approach to the bridge. This section was briefly described by Dr's C. E. Beecher, J. W. Hall and Mr. C. E Hall.\* In addition to the species mentioned, the writer found fronds of Archaopteris in the lower red shale near the railroad bridge, while still higher, in the zone of the Oneonta sandstone in the first R. R. cut north of the 218th mile post, are specimens of Amnigenia catskillensis (Van.) Hall, and plates of Holonema rugosa (Claypole) Newb.+ Between Oxford and the summit on the O. & W: R. R. and about one-sixth of a mile west of the 214th mile post, is a cut through red and greenish shales in which fossils occur as described in the above mentioned report. One-quarter of a mile east of the Summit in another R. R. cut are greenish and olive shales containing numerous fossils overlying the Oneonta sandstone.

A similar section may be constructed along the Susquehanna River from Oneonta to Bainbridge. In the Anthony White quarry, at the foot of the high hill just west of Oneonta, are abundant fossils that belong in the "Oneonta group" of Conrad, which continues up the hill for about 200 feet, the upper portion being composed of the Oneonta sandstone of Vanux-The rocks at the base of this hill, or Conrad's "Oneonta em. group," were correlated quite accurately by Vanuxem, who stated that he supposed them to belong to the "1thaca group."; Through the kindness of Dr. H. S. Williams I am able to quote from his Ms. list of the fossils collected in the Anthony

<sup>\*</sup> Fifth Ann. Rep. State Geologist [N. Y.] 1885, p. 11; see page 4 for credit.

<sup>+</sup> For an account of these plates see Dr. H. S. Williams in Proc. Am. Assoc. Adv. Sci., vol. xxxix, p. 337; Prof. Claypole in Am. Geologist, vol. vi, pp. 255-257, and Prof. Cope in Proc. U. S. Nat. Mus., vol. xiv, p. 456.
‡ Geol. N. Y.. Pt. III, p. 192. The clause reads, "the base of which [hill] is

composed of rocks which I have supposed to belong to the Ithaca group.

White quarry. The zone is called the *Paracyclas lirata* stage of the Hamilton fauna and its stratigraphic position was shown by Dr. Williams in 1885.\* A list of these species with their geologic range is given below.

	Fauna of Conrad's "Oneonta group" at Oneonta, New York.		Geologic Stage. <sup>+</sup>									
Number of Species.	List of Species.	Upper Helderberg.	Marcellus.	Hamilton.	Hamilton of eastern New York.‡	Portage.§	Ithaca	Oneonta.	Portage of eastern New York.	Portage of eastern Pennsylvania.**	Chemung.	
		1	2	3	4	5	6	7	8	9	10	
	Microdon (Cypricardella) bellistriata (Con.) Hall			×	×		×			 ×	×	
2	Paracyclas lirata (Con.) Hall			×	×			×	×	×		
3	Tropidoleptus carinatus (Con.) Hall			×	×	×		×	×	×	×	
	Palæoneilo maxima (Con.) Hall			××	××					×		
	Grammysia magna Hall Grammysia bisulcata (Con.) Hall			×	×		×					
	Cimitaria recurva (Con.) Hall (?)			×				×				
	Tellinopsis subemarginata (Con.) Hall			×	×			-				
	Modiomorpha concentrica (Con.) Hall			×	×		?					
10	Spirifera mucronata (Con.) Bill		×	×	×				?			
11	Goniophora carinata (Con.) Hall							×		?		
	Homalonotus De Kayi (Green) Emm		×	×	×				×	×		
13	Nuculites triqueter Con.		?	×								
14	Microdon (Cypricardella) gregarius Hall			×	×		×		×	×	×	
	Leptodesma Rogersi Hall			×	Υ.			×		?		
	Leiopteria De Kayi Hall			×	×							
	Orthonota undulata Con.			×	×							
	Microdon (Cypricardella) complanatus Hall			×	×			×				
		×		×	×							
20	Spirifera mesastrialis Hall			×	×	1	×		×	×	×	

\* Proc. Am. Assoc. Adv. Sci., vol. xxxiv, Chart of Meridional Sections of the Upper Devonian deposits of New York, Pennsylvania and Ohio, Section X, A'; where the *Paracyclas* fauna (A'), is shown immediately underlying the Oneonta reds and grays, (F'). † The data used in showing the geologic range of the species in the above list

<sup>+</sup> The data used in showing the geologic range of the species in the above list are derived principally from the various works of Professors Hall, H. S. Williams and Prosser. The distribution is confined to New York and eastern Pennsylvania which have been studied with such care that the evidence can be used with considerable force in this correlation. The range of a portion of the species reported from the Portage of eastern New York and Pennsylvania depends upon lists of the author, which have not yet been published. The horizon of this eastern fauna is clearly above the Hamilton, but we have not yet sufficient evidence to attempt its correlation with the different zones of the Portage in central and western New York.

<sup>‡</sup> The horizon of the species reported by Professor Hall, and some other authors, from the Hamilton of eastern New York is believed to require further investigation. The writer has evidence showing that a portion of these localities really Of the twenty species named in the above list fourteen are known to occur above the Hamilton, while five of the remainder are reported from the Hamilton of eastern New York, which as stated above needs revising since some of the so-called Hamilton horizons are in the Portage, and only one species so far as previously known occurred no higher than the Hamilton stage.

At Sidney, twenty-one miles southwest of Oneonta, the top of the Oneonta sandstone is reached in the hill forming the divide between the Susquehanna and Unadilla Rivers northwest of the village.

In Secor's quarry, about 140 feet above the railroad level at Sidney<sup>\*</sup> are grayish to olive standstones with greenish and bluish argillaceous shales. Plant and crinoid stems were found in the debris of the quarry, while near the top of the hill are loose slabs, with no indications of having been moved any considerable distance, containing poorly preserved specimens of *Leiorhynchus* and Lamellibranchs. At New Berlin Junction on the Ontario & Western R. R., two miles from Sidney, or at Bainbridge five miles down the Susquehanna River are numerous specimens of fossils which in both cases overlay the zone of the Oneonta sandstone.

The difficulty in correlating these deposits in which part of the stratigraphic series has disappeared and paleontologically many of the species common in the rocks below reappear in the higher rocks, in some cases unchanged and again slightly modified, may be overcome, it is believed, by carefully studying both the fauna and the stratigraphic relations of the rocks. This test has been made by the writer in southeastern New York and eastern Pennsylvania, where in the absence of the Tully limestone and Genesee shale, the problem is about the same as that presented along the Susquehanna River valley, and he believes it possible to separate the Hamilton from the overlying rocks of Portage age by the faunas contained in the respective stages.

belongs stratigraphically above the horizon of the Tully limestone and Genesee shale. Consequently it was considered best to give a separate column to those species separated from the Hamilton of eastern New York, some of which should probably be credited to the Portage.

 $\S$  Most of the species given in this column are from central and western New York.

|| Mainly from Ithaca and vicinity, forming the middle Portage of that region. ¶ This is the Oneonta zone of Conrad and the occurrence of the species at other localities than Oneonta, mainly from Norwich and Mt. Upton, Chenango County, is given.

\*\* The species reported from the Portage of eastern New York and Pennsylvania are mainly from my own lists.

\* Elevation of station at Sidney 992' A. T.

The Pennsylvania geologists have been inclined to call the upper stage Chemung,\* while some of the official geologists of New York have called the same rocks Hamilton, because certain species of fossils more or less common in the Hamilton stage occur in these rocks. At the Washington meeting of the International Congress of Geologists, a series of these fossils arranged in their stratigraphic order was exhibited to several geologists and Dr. H. S. Williams recognized the difference in age, thus proving that a careful study of these faunas will enable one to separate them.

In order to show the nature of this fauna, a list of the species noted along the Delaware River above Port Jervis, New York is given. From the Hamilton were obtained :---

2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22.	Spirifera granulifera Hall       (aa)         Spirifera mucronata (Con.) Bill.(aa)         Tropidoleptus carinatus (Con.) Hall         (aa)         Orthis Vanuxemi Hall         (a)         Chonetes coronata (Con.) Hall. (r)         Leiorhynchus multicosta Hall (r)         Chonetes setigera Hall         (c)         Nucleospira concinna Hall (rr)         Athyris spiriferoides (Eaton) Hall (rr)         Cyrtina hamiltonensis Hall (rr)         Palæoneilo constricta (Con.) Hall (r)         Nucula bellistriata (Con.) Hall (rr)         Nucula bellistriata (Con.) Hall (rr)         Palæoneilo maxima (Con.) Hall (rr)         Nucula corbuliformis Hall (rr)         Nuculites cuneiformis Con (rr)         Goniphora hamiltonensis (Hall) Mill.         (rr)         Muculites cuneiformis Con (rr)         Goniphora hamiltonensis (Hall) Mill.         (rr)         Microdon (Cypricardella) tenuistria-         tus Hall (?) (ron) Hall	$\begin{array}{c} 27.\\ 28.\\ 29.\\ 30.\\ 31.\\ 32.\\ 33.\\ 34.\\ 35.\\ 36.\\ 37.\\ 38.\\ 39.\\ 40.\\ 41.\\ 42.\\ 43.\\ 44.\\ 45.\\ 46.\\ 47.\\ \end{array}$	Grammysia bisulcata (Con.) Hall (rr) Cimitaria corrugata (Con.) Hall (rr) Actinopteria Boydi (Con.) Hall .(rr) Modiomorpha concentrica (Con.) Hall 
22.		47.	
23.	Tellinopsis subemarginata (Con.) Hall		Dalmanites (Cryphæus) Boothi
	(rr) Pholadella radiata (Con.) Hall(rr) Leda diversa Hall(rr)		(Green) Hall (?)(rr) Psilophyton princeps Dn(rr)

The fossils of the above list were all collected from exposures along the Delaware River or the neighboring hills not more than two and one-half miles above Port Jervis. The age of the formation is Hamilton, although it has been mapped and described as Hamilton and Genesee.<sup>+</sup>

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The next higher zone is well exposed along the south bank of the river both below and above the N. Y., L. E. & W. R. R. bridge, three miles northwest of Port Jervis. The following species were obtained from this locality :—

1. Spirifera mesastrialis Hall(rr)	6. Palœoneilo plana Hall(rr)
2. Palæoneilo emarginata (Con.) Hall	7. Paracyclas lirata (Con.) Hall. (rr)
$\dots$ $(rr)$	8. Grammysia subarcuata Hall (?) (rr)
3. Leda diversa Hall(r)	9. Modiomorpha subalata (Con.) Hall
4. Microdon (Cypricardella) tenui-	var. chemungensis Hall (?)(rr)
striata Hall (?)( $rr$ )	10. Actinopteria Boydi (Con.) Hall_(a)
Possibly it is <i>M. gregarius</i> Hall, but	11. Homalonotus DeKayi (Green) Em-
it resembles the former more closely.	mons
5. Orthonota carinata Con(rr)	

The zone from which the above species were obtained was called Chemung by the Pennsylvania Survey;\* still the fauna is not a Chemung but a modified Hamilton one and the zone belongs to the Portage stage of central and eastern New York.

It seems clear to the writer that the above lists of fossils with the statement of their stratigraphic position show that the fossiliferous zone underlying the Oneonta sandstone in Chenango and Otsego counties is not the top of the Hamilton but belongs in the Portage stage. It appears to be well established by careful study that the typical Hamilton fauna and the higher or modified faunas, when considered in connection with their stratigraphic position, may be traced for a long distance across eastern New York and Pennsylvania. The facts briefly described in this paper, which have required a considerable amount of investigation and study, are commended to the attention of those engaged in the preparation of the new geologic map of New York.

Topeka, Kansas, May, 1893.

\* *Ibid.*, p. 194, where it is stated that the Chemung commences about one-half mile above the Erie railroad bridge and continues down the river for nearly two miles. See also the geological map with the report.

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ART. XXXIV.—On the Estimation of Chlorates and Nitrates, and of Nitrites and Nitrates in one operation; by CHARLOTTE F. ROBERTS.

[Contributions from the Kent Chemical Laboratory of Yale College-XXVII.]

A RECENT paper by Gooch<sup>\*</sup> and Gruener has shown that nitrates may be estimated most accurately by treatment with manganese chloride, the chlorine thus liberated being collected in potassium iodide, and the amount of iodine set free determined by titration with sodium thiosulphate. In a late number of this Journal,<sup>+</sup> I have shown that good results are also obtained by treatment of the nitrate with ferrous chloride, and collecting and measuring the nitric oxide evolved over sodium hydroxide with the apparatus described and pictured in that article.

This apparatus consists essentially of a small retort fitted with a hollow, ground-glass stopper prolonged beneath in a tube, and joined above with two branching tubes through one of which carbon dioxide may enter, and the other of which is attached to a funnel-tube with stop-cock, through which liquids may be introduced without admitting air. The retort is connected with a small condenser, which in turn is attached to a Will and Varrentrapp tube containing potassium iodide, and this with a Hempel's burette containing a strong solution of sodium hydroxide. In the experiments described, the potassium nitrate was introduced into the retort, carbon dioxide passed through until the air was completely driven out, and then ferrous chloride added through the funnel-tube. After heating, and passing a current of carbon dioxide through the apparatus, the volume of gas unabsorbed by sodium hydroxide was measured at the observed temperature and pressure, and from this the weight of potassium nitrate was calculated. This is merely a special form of a very common method of estimating nitrates, but the apparatus is in a form which can be conveniently handled and which readily adapts itself to other uses beside the simple determination of nitrates. In a mixture of chloric and nitric acids, for example, it becomes possible by a combination of the two above-named methods for estimating nitrates, and the use of the apparatus described, to determine in one operation the amounts of each present. A method for the determination of chlorates which has long been in common use consists in treatment with hydro-

\* This Journal, vol. xliv, 117.† Vol. xlvi, p. 126, August, 1893.

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chloric acid, the liberated chlorine being conducted into potassium iodide, and the iodine set free determined by titration with sodium thiosulphate. This method is entirely analogous to the first mentioned method of determining nitrates, the only difference being that in the latter case a solution of manganous chloride in hydrochloric acid is used instead of the acid In case of the nitrate, however, there is a second alone. product, nitric oxide, which may be collected and measured. It would then seem possible, with the use of the apparatus heretofore described, to treat a mixture of a chlorate and nitrate with manganous chloride, pass the resulting gases through potassium iodide, and then into the Hempel's burette. The amount of nitric oxide will give at once the amount of nitrate present. The iodine liberated will give the total chlorine set free by the reduction of the nitrate and chlorate. After that which is due to the nitrate determined has been deducted, we have an exact measure of the chlorate present.

To verify these presumptions, a few preliminary experiments were first made with potassium chlorate alone. In these, and all of the following experiments, great care was taken that the escaping gases should only come in contact with glass. Between the condenser and Hempel's burette were two Will and Varrentrapp tubes sealed together and containing potassium iodide, and generally a Geissler bulb containing potassium iodide was also added to make sure that no chlorine escaped absorption. The potassium chlorate was weighed out and introduced into the retort, air driven out by carbon dioxide, and then manganous chloride added through the funnel-tube. The liquid became dark at once, and a short heating sufficed to restore it to its original clear, light-green color. When this was accomplished, a current of carbon dioxide was passed through the apparatus, the bulbed tubes were disconnected, and their contents titrated with sodium thiosulphate. The following results were obtained from five trials:

	Wt. KClO <sub>3</sub> taken.	Wt. KClO <sub>3</sub> found.	Difference.
(1)	0.1000	0.0330	0.0010
(1) (2) (3)	0.1000	0.0995	0.0002
(3)	0.0200	0.0484	0.0016
(4)	0.0200	0.0498	0.0005
(5)	0.0200	0.0496	0.0004

Working in the same way with a mixture of potassium chlorate and potassium nitrate, and estimating the amount of nitrate first from the nitric oxide produced, the following results were obtained :

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	W	eights taken.	Weights found.	Difference.
(1)	Potassium chlorate	0.0200	0.0515	0.0012
( )	Potassium nitrate	0.0200	0.0494	0.0006
(2)	Potassium chlorate	0.0200	0.0208	0.0008
(2)	Potassium nitrate	0.0200	0.0493	0.0007
(9)	Potassium chlorate	0.1000	0.0987	0.0013
(3)	Potassium nitrate	0.1000	0.0992	0.0002
(4)	Potassium chlorate	0.1000	0.1007	0.0002
(4)	Potassium nitrate	0.1000	0.0980	0.0020
(~)	Potassium chlorate	0.0300	0.0302	0.0002
(5)	Potassium nitrate	0.1000	0.0330	0.0010
$(\alpha)$	Potassium chlorate	0.1000	0.1006	0.0006
(6)	Potassium nitrate	0.0300	0.0293	0.0002

The method is simple, rapid, and easy, and sufficiently accurate for most analytical work. One objection that may be urged against it is that any error in the determination of the nitric acid involves a corresponding error in the amount of chloric acid, but the above results show that such errors will be quite small if the experiment is conducted with proper precautions.

It also appeared probable that a nitrate and nitrite could be estimated at one operation in a somewhat similar manner. By the action of manganous chloride on a mixture of nitric and nitrous acids, nitric oxide and iodine would be set free from each. Representing the weight of nitric oxide found by a, and the weight of iodine found by b, and letting x equal the amount of nitric acid operated upon, and y the amount of nitrous acid,

> $\frac{30}{63}x + \frac{30}{47}y = a, \text{ and}$  $\frac{379\cdot5}{63}x + \frac{126\cdot5}{47}y = b$  $x = 0.249 \ b - 1.049 \ a$  $y = 2.35 \ a - 0.186 \ b$

whence,

In the attempt to verify these formulas by experiment, a little difficulty was found in getting a pure and stable nitrite upon which to operate. Some silver nitrite was prepared by precipitation from potassium nitrite and silver nitrate. This was washed well and dried as thoroughly as possible over sulphuric acid in the dark. Weighed portions were put in the retort, and after the air was expelled, manganous chloride was added. The amount of silver nitrate was then estimated from the iodine set free in the bulbed tubes, and also from the nitric

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oxide left in the Hempel burette. The results varied from one another by 4 or 5 per cent on different portions, but a few trials were sufficient to indicate that the trouble lay in the silver nitrite and not in the process itself. The percentage of purity as obtained from several trials by ignition was 98.4 per cent. The average of ten trials estimating from nitric oxide gave 98.1 per cent, and from the liberated iodine 98.7 per cent. This was uniformity enough to indicate that the method of work was trustworthy, although there was apparently such a lack of homogeneity in the silver nitrite as to make it impossible to use it in testing the value of the formula given above.

To obviate this difficulty, more silver nitrite was precipitated, well washed, dissolved in warm water, and a solution of sodium chloride added. The silver chloride was then filtered off, and the resulting solution of sodium nitrite was used in the following experiments. To determine the strength of this solution, ten or fifteen cubic centimeters were drawn off from a burette, and the nitrite estimated with potassium permanganate according to the method of Kinnicutt and Nef.\* At the same time, similar amounts were introduced into the retort with manganous chloride, and the nitrite estimated both from the liberated iodine and the nitric oxide formed. It was found that the air must be thoroughly driven out of the apparatus before the nitrite was introduced, as the carbon dioxide, passing over the solution, decomposed it with liberation of nitric oxide which, in presence of air, gave an excess of free iodine, and at the same time a little gas was lost. Accordingly, carbon dioxide was first passed through the apparatus for some time, then the nitrite was introduced through the funnel-tube and rinsed in with a little water, followed by the manganous chloride solution, care being taken that the water should not exceed one-third of the total volume of the liquid, according to the precaution to be shown necessary by Gooch and Gruener. Working in this way with the solution of sodium nitrite, the following results were obtained :

	Vol. taken.	Weight reckoned from KMnO <sub>4</sub> .	Weight reckoned from NO.	Weight reckoned from iodine.
	cm.	grm.	grm.	grm.
(1)	10	0.0463	0.0456	0.0450
(2)	10	0.0460	0.0460	0.0420
(3)	15	0.0704	0.0208	0.0722
(4)	15	0.0690	0.0712	0.0720
(5)	15	0.0201	0.0204	0.0722
(6)	15	0.0688	0.0696	0.0692
(7)	15	0.0706		
(8)	15	0.0213		

\* Ann. Chem. Journ., v, p. 388.

It will be seen that the results reckoned from the iodine are in general larger than those obtained by either of the other methods. This is what might be expected on account of the difficulty of completely removing air from the apparatus and solutions employed, and such air would naturally cause an excess of iodine. In (4) especially it will be noticed that we have an abnormally large amount of iodine set free, and this may undoubtedly be attributed to air, since it was observed that the current of carbon dioxide was rather sluggish at the time of that experiment.

The average of the above-recorded experiments would give as the value of fifteen cubic centimeters, from the method of Kinnicutt and Nef, '0697 grams, from the nitric oxide, '0699 grams, and from the iodine '0711 grams. If we assume that the mean weight per fifteen cubic centimeters is represented by the average of these three modes of determination, we obtain 0.0702 grams, and that is the number which is used in the following determinations to represent the weight of sodium nitrite in fifteen cubic centimeters of the solution. The following experiments were made in the same way as the preceding, except that potassium nitrate was introduced in the dry state before the air was driven out of the apparatus, and the results were calculated from the formula given above.

		Weights taken.	Weights found.	Difference.
(1)	Sodium nitrite	0.0702	0.0218	0.0016
(1)	Potassium nitrate	e 0.1000	0.1000	0.0000
(0)	Sodium nitrite	0.0202	0.0712	0.0012
(2)	Potassium nitrate	e 0·1000	0.0999	0.0001
$\langle n \rangle$	Sodium nitrite	0.0202	0.0710	0.0008
(3)	Potassium nitrate	e 0.1000	0.1004	0.0004
$\langle A \rangle$	Sodium nitrite	0.0202	0.0698	0.0004
(4)	Potassium nitrate	e 0.1000	0.1012	0.0015
(=)	Sodium nitrite	0.0468	0.0423	0.0013
(5)	Potassium nitrate	e 0.1000	0.0994	0.0006
(c)	Sodium nitrite	0.0468	0.0444	0.0024
(6)	Potassium nitrate	e 0.0200	0.0213	0.0013

Though the process is one in which the most perfect accuracy cannot be assured in all cases, the above results show that it is capable of giving fairly accurate results, sufficient for many analytical purposes. It seems to be especially well adapted to the estimation of the commercial alkali nitrites, the whole determination being made on one portion and by one operation, instead of on two different portions.

### ART. XXXV.—Alphonse DeCandolle.

ALPHONSE LOUIS PIERRE PYRAMUS DECANDOLLE, the son of Augustin Pyramus DeCandolle, was born on the 28th of October, 1806, and died in his eighty-seventh year, on the 4th of last April (1893). His father, born in 1778, published his first botanical work in 1799; thus the scientific activity of these two remarkable botanists covers nearly a full century.

Casimir, the son of Alphonse, has contributed not only to systematic botany but also to the philosophy of the subject, in striking treatises on leaf arrangement and on the morphology of the leaf itself. There are therefore three generations of botanists, by the last of whom the century is, we may hope, to be more than rounded out.

Augustin, of the first generation, was widely known for his concise and clear exposition of the fundamental principles of vegetable morphology, as well as for his comprehensive endeavor to describe all known flowering plants. It is interesting to note that in the same field of exposition, Alphonse, of the second generation, began his philosophical work. The Théorie Élémentaire of the father is fitly followed by the Traité Élémentaire of the son. The latter treatise, commonly known as the Introduction, was published in 1835, in two volumes covering the essential principles of pure and applied botany. An unauthorized edition, in one volume, was published in Brussels, in 1837, and the work has been translated into the principal continental languages. Those who look carefully into this compact treatise, knowing what its author subsequently accomplished, will see clear indications of symmetrical development, together with a marked tendency to investigate speculative aspects of the different branches of the subject. One phase of the subject possessed for him such strong attraction that he published, one year later, than the Introduction, a small work on the Distribution of Foodplants. Thus while aiding his father in the elaboration of the natural orders for the Prodromus, he was engaged in attacking philosophical questions of the greatest importance. We must say once for all that his interest in Systematic Botany, as evinced in the countless pages either written or edited by himself, did not flag even up to the very last; but with all this extraordinary activity in Systematic Botany, he was busy with every conceivable collateral speculation, always so bold and yet conservative, as to keep the confidence even of those who could not follow him. This speculative tendency is shown most strikingly in the great Botanical Geography, published by him in 1855. This vast work consists of well arranged facts brought together with untiring assiduity from all possible quarters. As the first volume draws to its close, it is seen that the clue which the author

thought he had well in hand has failed him, and from that time on there is hint after hint of some new way out of the difficulty of accounting for apparent caprice in the distribution of plants. Now that one can read his work in the light which has come from the luminous suggestions of Darwin and of Wallace, we can easily understand how gladly the author accepted the hypothesis of derivation through Natural Selection. From our point of view we can now see how near he came to making this fertile suggestion himself; one can almost believe that at times he had the very clue in hand. His acceptance of Darwinism, as he understood it, was unreserved, but it was not always the Darwinism of Darwin. In regard to the two important matters, of inheritance of acquired characters, and of vagueness or directness in development, he entertained views which are not accepted by some of Mr. Darwin's followers; but he claims that his interpretation is justified not only by the facts, but by Mr. Darwin's These views are presented with remarkable perown words. spiculty in a work on the History of two Centuries of Science and of Scientific Men. This treatise is preceded and followed by studies on other subjects, particularly in regard to Natural Selection as applied to man. This work was first issned in 1873: a revised edition followed after the lapse of twelve years. During that time he had not changed his opinions to any great extent, but he had the satisfaction of withdrawing from the second edition, as unnecessary, a defence of Darwinism which he had made in the first, because in 1885 among his French contemporaries he stood no longer alone as a Darwinian. He accomplished in France what Dr. Gray effected here, and Bentham and Hooker in England, namely the conversion of botanists to the belief that in Darwinism is found a safe working hypothesis by which one can account for the anomalies in distribution.

A word respecting some of the other subjects discussed in the volume devoted to the History of Science may be given conveniently at this point. These titles are, (1) Concerning observation of facts in schools and later. (2) On observation of social facts. (3) On statistics. (4) On the influence of heredity, variability, and selection in the human species, and on the probable future of this species. (5) On alternations in the intensity of epidemics, and in the value of prophylactic measures against them. (6) Which of the modern languages will be the dominant one in the 20th century? (His answer is, English.) (7) On the different meanings of the word "nature" and its derivatives. The chief essay, which gives its name to the volume, On the History of Science and Scientific Men for two Centuries, is devoted to a discussion of the influences exerted by surroundings, such as country, climate and social conditions, on the production of scientific men. It is, in short, a social study, somewhat after the type of Mr. Galton's English Men of Science, their Nature and Nurture. He makes a broad distinction between the faculties of a high order which are attributable to heredity and those which

manifest themselves for the first time in a family, and are to be regarded as individual variations. This briefest possible analysis of the volume on History indicates sufficiently the wide range of DeCandolle's inquiries, but it cannot give even an intimation of the marvellous charm of style of which he was a master.

We turn now to a consideration of his Phytography. A work designed to give instruction in methods of describing plants would be thought necessarily technical and dry. But every page of this work possesses attraction not only for botanists but for students in all fields of thought. The methods which he deals with are applicable, mutatis mutandis, to other branches of science. He gives many hints as to methods of accumulating facts from different sources, and imparts as far as one can do so, the secret of winnowing wheat from the chaff. He lets us into the mysteries of his cabinet, in which he stored myriads of facts for his systematic treatises and for his geographical botany. Our readers will hardly agree with all his views as to the relative value of different appliances for botanical research, but every one must be struck by the fairness with which personal views are presented.

In 1883, appeared his treatise on the Origin of Cultivated Plants. This has been translated in the so-called International Series and is doubtless familiar to all of our readers. It illustrates the extraordinary scope of his observation and reading, and his judicial method.

We have deferred until the last a notice of his Laws of Botanical Nomenclature. At the Paris International Botanical Congress, held August 16-26, 1867, he presented for consideration a system of rules to govern botanical nomenclature. This body of laws was discussed first by a special committee, and then by the whole Congress. With some modifications the system was adopted. The Code, accompanied by a commentary, was published by De-Candolle that autumn; sixteen years later, he published (1883) amended laws, together with some suggested changes, and a concise review of the discussions to which the laws had given rise.

Article 15 relates to the vexed question of priority. It reads, "Each natural group of plants can bear in science but one valid designation, the most ancient, whether adopted or given by Linnæus, or since Linnæus, provided it be consistent with the essential rules of nomenclature." According to this, DeCandolle would make for generic names a fixed date, 1737, that of the publication of the first edition of the Genera plantarum : while species should date from the publication of the first edition of the Species plantarum, namely, 1753.

Carried out to its logical conclusions and without regard to conservative and traditional usage, this has opened the door to the introduction of what may well be deplored as unnecessary confusion. That which was dreaded by many has already happened : already there are at least two schools among those who have cut loose from traditional methods and have adopted certain dates or one date only as the point of departure in priority. The chaotic condition preliminary to a cosmos is fairly upon us. Exactly when and how and where from this confusion an orderly arrangement can arise it is at present impossible to tell.

Certain it is that all botanists would do well to preserve, throughout the present and the coming days of disorder, that freedom from prejudice which characterized all of Alphonse DeCandolle's work. If everyone, who rushes in fearlessly to take a hand in changing the names of plants, would bear in mind the cautions given in the Phytography, it would save many from mortification when the time comes for exact and enduring work to be sifted from that which is hasty, superficial and ephemeral.

G. L. G.

### SCIENTIFIC INTELLIGENCE.

### I. GEOLOGY AND NATURAL HISTORY.

1. Minnesota Geological and Natural History Survey.—A notice of the publication of the memoir of E. O. ULRICH on the Bryozoa of Minnesota, constituting a part of volume III of the final Quarto Report of the Minnesota Geological Survey, is given in the last volume of this Journal. More recently, the following parts of the same volume have been issued:

Sponges, Graptolites and Corals from the Lower Silurian of Minnesota, by N. H. WINCHELL and CHARLES SCHUCHERT. 42 pp. 4to, with 2 plates.

The Lower Silurian Brachiopoda of Minnesota, by N. H. WINCHELL and CHARLES SCHUCHERT. 144 pp. 4to, with 6 plates.

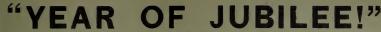
Prof. Winchell's Twentieth Annual Report for the year 1891, published during the current year, contains a paper by him on the Crystalline rocks, containing "some preliminary considerations as to their structure and origin," and another of 70 pages on the Mesabi Iron Range; Field observations on certain granite areas by N. S. GRANT; a paper on the abandoned strands of Lake Superior, 110 pages, with many illustrations, by A. C. LAWSON; on the Diatomaceæ of Minnesota in interglacial peat, by B. W. THOMAS, with a list of species and notes by H. L. SMITH.

THOMAS, with a list of species and notes by H. L. SMITH. 2. Paleontology of New York, Volume VIII, Part 2, Fascicle 1, by Prof. JAMES HALL, assisted by J. M. CLARKE. 176 pp. 4to. —This new part of Vol. VIII contains a continuation of Professor Hall's "Introduction to the Study of the Genera of the Palæozoic Brachiopoda." The names of the accepted genera and subgenera here discussed and described are Spirifer, Cyrtia, Cyrtina, Syringothyris, Spiriferina, Ambocelia, Metaplasia (n. g.), Whitfieldia (n. g.), Hyattella, Dayia, Hindella, Meristina, Merista, Meristella, Charionella, Pentagonia, Camarospira, Athyris, Cliothyris, Actinochonchus, Seminula, Spirigerella, Kayseria, Retzia, Rhynchospira, Ptychospira (n. g.), Uncites Eumetria, Acambona, Hustedia (n. g.), Uncinella, Trematospira, Parazyga, Anoplotheca, Cœlospira, Leptocœlia, Vitulina, Anabaia, Nucleospira, Cyclospira (n. g.), Glassia, Zygospira, Catazyga (n. g.), Atrypina, Atrypa, Gruenewaldtia, Karpinskia. Other names appear in the very full synonymy. Many figures of distinguishing characteristics are given in the text, and plates xxi to lii are referred to which will be contained in the completed volume.

3. Salt and Gypsum Industries of New York, by F. J. H. MERRILL, Assistant State Geologist. Bulletin of the N. Y. State Museum, vol. iii, April, 1893, 90 pp. 8vo, with maps, plates and sections.—Prof. Merrill treats briefly of the geological part of his subject, and illustrates it with maps showing the distribution of salt and brine wells as ascertained by borings. The economical subjects are discussed with great fullness and with numerous illustrating plates and figures.

4. Bionomie des Meeres: Beobachtungen über die marinen Lebensbezirke und Existenzbedingungen; von JOHANNES WAL-THER. First part, an Introduction to Geology as a historical science. 196 pp., 8vo. Jena, 1893 (Gustav Fischer).-Professor Walther, of Jena, treats in this very instructive volume, in a concise and systematic way, of the conditions of existence and range of marine life, with reference to the bearing of the subjects on geology. Some of the topics discussed, and illustrated by citations of physical and biological facts, are the following: The marine conditions connected with the arrangements of the continents, with their bays, estuaries, etc., and with the oceans, of varying depths, from the coasts downward, and of varying temperatures and varying kinds of sea-bottom and other living conditions; the influence of light and heat on growth and distribution; of salinity (with relation to which the author divides marine animals into the Stenohaline, or those requiring waters having the normal salinity of the ocean, the Euryhaline, or those capable of enduring a wide range, from brackish water to the normal, and the Brack-water, or those of brackish water); the influence of tides and waves; of currents and the general circulation; and many other points of special geological importance. Students in geology would profit much by the careful study of Prof. Walther's work. It promises well for the future parts of his Introduction to Historical Geology.

5. North American Fauna, No. 7. The Death Valley Expedition: a Geological survey of parts of California, Nevada, Arizona, and Utah.—Part II, containing Reports on different departments by A. K. FISHER, L. STEJNEGER, C. H. GILBERT, C. V. RILEY, R. E. C. STEARNS, C. H. MERRIAM, T. S. PALMER. Published by authority of the Secretary of Agriculture. 394 pp. 8vo, with 14 plates, 1 large map and 4 small maps illustrating geographical distribution.



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#### THE

### AMERICAN JOURNAL OF SCIENCE

### [THIRD SERIES.]

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### ART. XXXVI.—On Endothermic Reactions effected by Mechanical Force; by M. CAREY LEA. (Part First.)

In a preceding paper the effects of pressure on the silver haloids were described. These salts were readily blackened and so gave evidence of partial reduction. That investigation was undertaken with the object of bringing into complete harmony the effects upon these haloids of the different forms of energy. It had been previously shown with respect to all the other forms of energy that a slight impression made upon the haloids caused an effect not visible to the eye but capable of indefinite increase by the application of a reducing agent. Also, it had been shown in the case of mechanical force that a slight application would cause an invisible effect which could be rendered evident by the application of a reducing agent. It seemed to follow almost necessarily that a powerful application of the same agent would bring about an effect visible to the eye. Experiment proved this to be the case.

It next appeared worth while to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. For the nature of these changes was something quite different from anything that had been previously described. In Prof. Spring's well known investigation, combination was brought about between substances whose tendency to combine was restrained by their being in the solid form. This obstacle was removed by subjecting them to great pressure, and the same remark applies to some of the interesting experiments of Dr.

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Hallock. But the reduction of the silver haloids and other reactions presently to be described involve a quite different principle. The reactions produced are all endothermic; energy is consumed in accomplishing them and this energy is supplied by mechanical force.

The combination of screw and lever affords the best means of applying pressure. A careful study as to the most suitable method of using these powers led to the selection of the vise form. It was found, however, that the manufacturers of heavy vises were unwilling to undertake to furnish vises with jaws that would sustain the force intended to be exerted on them, namely, that of a steel lever three feet long acting on a screw with six turns to the inch. I was therefore obliged to have them made under my own supervision. From a bar of tough rolled iron 4 inches wide by  $1\frac{1}{2}$  thick, pieces about 18 inches long were cut and were forged into shape by a blacksmith; where the jaws met they were faced with steel welded Suitable screws were easily obtained, but the nuts furnished with them having commonly only an inch in length would subject the thread to the danger of stripping. They were replaced with nuts 4 inches in length, thus distributing the strain over 24 turns of the thread. Two vises made in this way over a year ago have endured severe use without the least sign of strain.

With a lever having three feet in length between the center of the screw head and the end at which the force is applied acting on a screw with six turns to the inch, the multiplication of force is 1357 times. As it is easy to apply a pull of a hundred pounds or even much more, a pressure of 135,000 lbs. is easily obtained. As it was intended to keep the substances which were to be subjected to pressure from any contact that might affect them they were folded up in platinum foil and this was set in a V-shaped piece of soft sheet copper. The portion of material which received the pressure was about  $\frac{1}{2}$  inch long by  $\frac{1}{4}$  wide; it consequently had an area of about <sup>1</sup>/<sub>4</sub> of a square inch. This limited surface received a pressure in the proportion of over a million pounds to the square inch or about seventy thousand atmospheres. These of course are calculated pressures subject to deduction for friction. The amount lost in this way cannot be determined but is known to be considerable.

By the aid of these means the following results were obtained. In all cases the material was wrapped in either platinum or silver, usually platinum, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

Silver sulphite in platinum foil was moderately darkened by two days pressure.

Silver salicylate was rendered very dark by two days pressure.

Silver carbonate was moderately darkened by a somewhat longer pressure.

Silver tartrate was not affected.

Silver oxide was thoroughly dried at 150°. A piece of platinum foil was heated to redness and rapidly cooled, a portion of oxide was folded up in it and weighed. Weight found '7639. It was then subjected to very great pressure for four days. Weight found to be '7639, no change.

*Ferric oxide* recently precipitated and dried. No effect produced by pressure, no formation of ferrous oxide.

Potassium platinobromide. Where the pressure was greatest the brilliant red color of this substance was blackened, not superficially only, but all through.

Ammonium platinochloride. Moderate but well marked darkening.

*Potassium chlorate.* When this substance was subjected to pressure by itself no effect whatever was produced and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder, and subjected to pressure there was an evident formation of silver chloride. The material was no longer completely soluble in water but left an abundance of white flakes which darkened when exposed to light.

Mercuric oxide requires a very high pressure to produce an effect upon it. It then darkens slightly but very distinctly and this change seems to be accompanied by a slight loss of weight requiring, however, very careful weighing to detect it.

The darkened part as well as the rest dissolves without difficulty in acetic acid and consisted therefore probably of traces of mercurous oxide and not metallic mercury.

Mercurous chloride showed no change.

*Mercuric chloride.* Corrosive sublimate perfectly free from calomel, which commercial sublimate is very apt to contain, was subjected to great pressure and then treated with ammonia. As no darkening took place there had evidently been no reduction.

*Mercuric iodide.* Red mercuric iodide when subjected to very great pressure darkened considerably and at points where the pressure was greatest it became absolutely black. It did not appear however, that any iodine was set free, none could be extracted with alcohol.

Mercuric oxychloride, 2HgO, HgCl<sub>2</sub>; heavy pressure caused much darkening.

Sodium thiosulphate with a moderate pressure compresses to a hard translucent cake but does not undergo any decomposition.

To the foregoing cases are to be added those of the three silver haloids described in a previous paper; these blackened with a quite moderate pressure even in the case of the iodide.

Although in all these instances the darkening is well marked, still the actual proportion of material affected is small, so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done and we are justified in concluding that many of the salts of easily reduceable metals, especially of silver, mercury and platinum, undergo reduction by pressure. Such reactions are endothermic and *it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force precisely in the same way that light, heat and electricity supply energy in the endothermic changes which they bring about.* 

In the second part of this paper additional support will be adduced for these conclusions.

August, 1893.

ART. XXXVII.—Studies on the Chipola Miocene of Bainbridge, Georgia, and of Alum Bluff, Florida, with an attempt at correlation of certain Grand Gulf group beds with marine Miocene beds eastward; by AUG. F. FOERSTE.

THE Miocene strata of Georgia, Florida and Alabama can be divided quite conveniently into three groups. Beginning with the older, these would be called in northwestern Florida, the Chattahoochee, Chipola, and Chesapeake Groups. The Chattahoochee contains an assemblage of fossils decidedly Miocene. A considerable number of forms have close affinities with those of Chipola age, while a decidedly less close relationship is found to exist with forms from the Vicksburg Eocene, at least as far as could be determined by comparison with those Vicksburg fossils actually discovered by us in southwestern Georgia. The facies of the Chipola fauna is decidedly southern, sub-tropical in fact, and there are many species identical with or closely allied to Miocene forms of regions bordering on the Caribbean Sea. The Chesapeake fauna, as its name was intended to imply, has however a decidedly northern facies, though the species are chiefly such as have long been known to exist in the South Carolina and North Carolina Miocene.

Alexander Agassiz has shown that in later Mesozoic times the Gulf of Mexico was probably connected with the Pacific across Central American regions, and the paleontological evidence favors the idea that this connection was not terminated until the close of the Eocene. The subsequent rise of the Central American ranges must have shut off a western outlet to sub-equatorial currents, and such currents as then entered the present Gulf region were obliged to find an outlet by curving along the western and northern shores until they found an exit, as does the Gulf Stream of to-day. This early Miocene return-current, however, is shown by Mr. W. H. Dall\* not to have passed to the south of the peninsular portion of Florida, but to the north of it, between present peninsular Florida and Georgia. For convenience in terminology the return-current may be called the Okefenokee current, and the passage, the Okefenokee straits.

Mr. Dall\* shows that towards the end of the Eocene a part of peninsular Florida had already been raised above the sea, and that during the deposition of the Nummulitic or very late Eccene beds, "this elevation (probably in the form of a chain of islands), had continued long enough for these islets to acquire a landshell fauna, as far south as about latitude 29° north." This group of islets of central Florida having a similar geological history may be conveniently termed the Ocala islands. The area occupied by these islands was increased during the earlier Miocene, and their continuous history is suggested by the presence of forms in the upper part of the Orthaulax beds, identical with those already mentioned as occurring in the late Eocene of this region. North of the Ocala islands the very wide Okefenokee passage must have been shallow at first, as is suggested by the fact that the Chattahoochee does not immediately introduce as southern a type of fauna as is contained in the later or Chipola beds, when the passage was probably deeper and the return current more vigorous. The Chipola fauna with its decidedly sub-tropical, Antillean or Caribbean facies, extended all along this passage as far as the Atlantic, and thence some distance northward.

A great deflection of currents took place at the close of the Chipola.\* Instead of the eastward flowing warm water Okefenokee current, the southwestward-running Chesapeake or cold

\* Correlation Papers. Neocene. See also publications of Mr. L. C. Johnson.

water current seems to have split near the northeastern part of present Florida, and while a part flowed along the eastern and southern margins of the then greatly extended Ocala islands, another part passed by way of the Okefenokee passage to the westward and permitted a cold water fauna to extend all along the southern border of the Miocene continent, almost coincident with present northern Florida, so that the two faunas Chipola and Chesapeake, though probably to a considerable extent contemporaneous, in point of time, are stratigraphically very distinct here and represent different geological ages for this southern area. How completely changed the forms of life became by this deflection of currents, can only be appreciated by one who has had the good fortune to collect along the Appalachicola and Chipola rivers.

Fossiliferous exposures of Chipola age north of the well known localities at Alum Bluff and south of Bailey's Ferry are known only at one place, half way between Bainbridge and Fowltown in Georgia and thence eastward for some distance. These localities discovered by Professor Raphael Pumpelly \* are about 40 miles northeast of the Alum Bluff exposures, and represent a northing of about 22 miles across the strike. Their chief interest lies in the fact that they represent the extreme northern limit to which the Chipola current was able to penetrate; they are in fact immediate off-shore deposits. This is shown not only by the very comminuted and strongly washed and rounded shell fragments which characterize these horizons, often making their determination very difficult, but also by the presence of pulmonate land shells : an undoubted *Helix* and an apparent *Bulimulus* as indicated in the list given later.

Another point of interest consists in the fact that these fossil localities have recently been shown by the still unpublished work of Prof. Pumpelly to constitute a definite horizon in the red clay hills of the region, overlying the Chattahoochee formation which constitutes the lower portion of these hills. Now these red clay hills form a part of a great series becoming a sort of plateau in southwest Georgia and adjacent Florida, and having those lithological characteristics which would lead them to be classified as Lafayette clays, where the determination of the Lafayette is not the result of detailed work over areas not too large to prevent definite correlation. It is becoming evident in consequence of Prof. Pumpelly's stratigraphical studies that the red clay hills of this country characteristically present Chattahoochee at the base, Chipola higher up, still higher horizons representing undoubtedly the Alum Bluff sands, and whether any higher horizons are present remains to be determined.

\* W. H. Dall, Correllation papers, Neocene; under Georgia.

The often sandy clays overlying the Chipola of this red clay hill region from Bainbridge southward are undoubtedly to a considerable extent perezonal material, becoming coarser towards the unfossiliferous Chattahoochee embayment of Chipola times. What this means will be better understood when it is learned that in Florida the Chipola also ends above in a mass of perezonal sands, the feather edge of the much thicker northern deposits. These perezonal sands, moreover at Alum Bluff, contain in places frequent impressions of palmetto and many dicotyledonous leaves, showing a great Gulfward extension of continental land before the deposition of the Chesapeake. This may account in part for the fact that while the Chipola has been found farther north, the Chesapeake can be traced only a short distance north of Alum Bluff.

Previous publications with reference to the position of the leaf remains, if correctly understood, are entirely erroneous. At Alum Bluff the Chipola rises only a few feet above the river's edge under ordinary conditions of water level. Below they consist of a strongly calcareous sandy formation, calcareous chiefly on account of its abundant shell remains; becoming a loose sand layer above as soon as the fossils practically disappear. This upper sandy portion may be almost structureless and contain a few gasteropods and oyster shells, or it may be strongly cross-bedded, when it is likely to contain trunks with more or less of the leaves of palmetto palms, or they may be finely interbedded with thin more clayey layers, when they are more apt to contain the best specimens of the dicotyledonous leaves. In the few localities studied the cross-bedded sands lie over the evenly bedded leaf layers last mentioned, and the stray oyster shells are found some distance away horizontally, at various levels. These formations all evidently form a unit and signify simply that towards the close of the Chipola a considerable area was added to the land and the effects are recognized as far south as Alum Bluff in the form of land plant containing deposits. (It will be remembered that earlier in this paper the writer notes the similar observation of Dall when he states that towards the upper part of the equivalent Orthaulax bed a *land* shell fauna comes in). Above these leaf-bearing sands at Alum Bluff the Chesapeake formation is found.

To every one familiar with Southern geology it is evident that Tertiary rivers here have given rise to great perezonal deposits. Stratigraphically the Altamaha grits some distance south of central Georgia and the Grand Gulf group of the Mississippi embayment should represent such perezonal deposits for the entire Miocene, since they rest directly upon the Eocene. Only recently has an attempt been made to subdivide the Grand Gulf group and to correlate its members with the marine Miocene deposits farther east.

Mr. Lawrence C. Johnson, to whom the writer is indebted for the most of the following information,\* has been enabled to divide the Grand Gulf group into four phases: A basal quartzitic phase called the Bayou Pierre phase developed chiefly towards the Mississippi river; a second, called the Fort Adams or Ellisville phase which has been traced eastward into Alabama; an upper or Hattiesburg phase, abounding in phytogene remains which has also been traced into Alabama; and a fourth or Pascagoula phase which in its eastward extension has. been found only in borings in Mobile County at the southwestern corner of Alabama.

The Hattiesburg or phytogene phase is well developed in Mississippi at Rawl's Springs and the shoals of Bouie river near Hattiesburg; at Coal Bluff, near Augusta, on Leaf river; at Powe's Bluff on the Chickasawhay river, above Lakeville; at Shell Landing, below Roberts' Bluff, four miles southwest of Vernal; extending thence into Alabama, occupying the southern part of Washington County, occurring, for instance, on the southern branches of Bassett's creek, where crossed by the St. Stephens and State Line road; thence across northern Baltimore into Escambia County where the Conecuh river and its tributaries expose this phytogene phase near Castleberry on Murder creek; at Coal Bluff, seven miles south; at Silas Bluff, on the Conecuh, six miles east; and at Roberts' on Silas creek, not far eastward.

At the last locality, Roberts, occurs an exposure which seems to be of considerable importance for purposes of correlation. Here "the bluff washed out by the waste-way of the mill is filled with the casts of fossils." Mr. Johnson informs me by letter that Mr. Dall thinks these fossils indicate the lowest or oldest Miocene. "The wood and lignitic matter" or Hattiesburg phase, occurs "in the upper part of this wash-out bluff." The most northern outcrops of the Chesapeake in this vicinity seem to be at "the low shell landing on the Yellow River at Oak Grove, six miles south of the Alabama line."\*

In a general way it seems to be possible therefore to establish a correlation between the Miocene of the Appalachicola embayment region, and that of the eastern margin of the Grand Gulf Group. Correlating the phytogene or Hattiesburg phase of the Grand Gulf at Roberts with the leaf-bearing sands at the top of the Chipola at Alum Bluff, the Ellisville and lower horizons of the Grand Gulf Group of this vicinity should correspond to the marine Chipola and the Chattahoo-

\* Science, Feb. 17, '93, and personal correspondence.

chee formations eastward; and the Oak Grove horizon should correspond to the Chesapeake horizon of Alum Bluff at least to the extent of representing the later Miocene of this area.

Mr. Johnson in his letter mentions only Euchee Ana in Walton Co., Florida, as a more eastern phytogene locality. The connection between the Roberts phytogene locality and the Alum Bluff bed is therefore not determined by as frequent intermediate localities of that description, as could be desired. The better known course of the upper or Chesapeake Miocene must be therefore relied upon (in addition to the correlation evidence just given) to establish the continuity of the lower horizons.\*

The difficulties which are at present being found to distinguish between the horizons of the more western Miocene localities will be better understood if the effects of two such different currents as the Chipola and the Chesapeake currents are considered. During the deposition of the Chattahoochee along the Appalachicola embayment, the southern current does not seem to have brought in as yet a great quantity of southern or Chipola types. From the nature of this current the fauna would be introduced into this embayment from the west, and in the western localities an intermixture of Chattahoochee and Chipola fossils might occur, while a more rapid introduction of the Chipola fauna at some later date into the Appalachicola region would make the change there more sudden, and the two faunas would be more distinct in this eastern embayment. At Alum Bluff the later history of the Chipola is that of a formation containing chiefly phytogene remains. During this later period of the Chipola the Chesapeake fauna was being introduced from the northeast, but owing to the phytogene phase at Alum Bluff the intermixture of Chipola and Chesapeake fossils is not shown here, and by the time that marine waters again covered Alum Bluff the southern fauna had been excluded by the Chesapeake current. Towards the west, however, this transformation of faunas may not have been so complete at the close of the phytogene phase, in fact

\* The difference between the correlation here attempted and that suggested by Mr. Johnsou, in his paper on the Miocene group of Alabama, loc cit., is that the Alum Bluff plant containing deposits being considered at that time of post-Chesapeake age, it was necessary on the basis of any true principles of correlation to classify the phytogene deposits of Alabama, if at all, as post-Chesapeake, instead of pre-Chesapeake, hence Mr. Johnson's desire to classify the fossiliferous deposits at Roberts as the Chesapeake (Alaqua phase) instead of the lowest Miocene, as he informs me Mr. Dall interprets the same. A marginal pencil note by Mr. Johnson to this passage adds "mixed with some of older time of Chipola" fossils suggesting the possibility that Chipola as well as Chattahoochee fossils may be present below the phytogene deposits of Alabama. On the basis of present views the true Chesapeake deposits of Alabama must be expected above instead of below the Hattiesburg phytogene phase. How far these views are correct will have to be shown by future studies. the cold water current may never have been strong enough to totally exclude the warm water fauna so far westward, and hence an intermixture of Chipola and Chesapeake faunas with a decrease of the cold water elements must be expected on going westward beyond the sphere of strongest influence of this current. Finally, the phytogene phases being of course a fixed horizon only relatively, showing only a general concordance of continental development southward, it may be, that while the Alum Bluff region was receiving phytogene perezonal deposits, the invading Chesapeake fauna of this time, although excluded from the Alum Bluff area, passed by to the southward, and reached western areas before certain localities in this western region had assumed the phytogene phase. This would be quite naturally the case if the elevation of the Chipola land was more pronounced eastward in the Appalachicola area, than westward in the Yellow River region. The result would be the introduction of a Chesapeake element into the Chipola fauna at a time preceding the phytogene stage of these western regions. In this manner a certain commingling of Chesapeake and Chipola types might be expected to exist both in the formations preceding and in those following the phytogene phase westward. With a full understanding of all of these possibilities it may be possible to establish in the future on the basis of detailed work, some such correlation between the Miocene horizons of the Appalachicola embayment and the various members of the Grand Gulf group, as that suggested in the preceding lines, on the results of the present stage of knowledge, and in consequence partly of the discovery of the phytogene character of the upper Chipola sands at Alum Bluff. It is hoped these observations may encourage further investigation and not be considered final.

The Chesapeake formation at Alum Bluff merges at the top into a few feet of a dark looking clay, the burrowing places of thousands of mud-burrowing bees, in which clay occur Chesapeake fossils, in some places rather plentifully. While of course it would be useless to deny the total absence of phytogene remains here, since negative evidence is never final, it should be said that the writer made two trips to this region, one for the special purpose of determining this question, and while there was no trouble in tracing the loose palmetto leaf and other remains to the Upper Chipola sands and their interlaminated clays in the cliffs above, where they occur *in situ*, in no instance was any leaf or stem found by us in the peculiar dark clays which terminate the Chesapeake at this locality.

· ·	e	C for		oola tior		1		
A provisional list of the Gasteropod Gully species with a comparative study of their distribution south- ward, as well as their history in Chattahooche and Chesapeake times.	Chattahooche formation.	Gasteropod Gully.	Alum Bluff.	Bailey's Ferry.	Okeetoksu Bluff	Alum Bluff, Chesapeake.	Horizons of Types.	Publications.
Ostrea divaricata, Lea, 1	?	*	?	?			Claiborne.	1
Pecten Madisonianus, Say, 2	Ъ	*					{ Chesapeake. } Older Maryland.	2
Arca idonea, Conrad	a *	*	*	*	* ?	*	Chesapeake.	2
Cardita [Carditamera] protracta, Conrad, 4		*	*		*		Chesapeake.	2
Venus, var. of mercenaria, small, 5_	*	*			*		Ohaanaalaa	3
Strigilla flexuosa, Say		*					Chesapeake. Chesapeake.	$\frac{5}{2}$
Solen ensis, Linné, 6	a	*				Ъ	Chesapeake.	3
Conus planiceps, Heilprin, 7 Drillia lunata, Lea, 8	a	* * *	*	*	*	α	Chipola. Chesapeake.	4
Drilha, 3 species		*	?				∫ Chipola. } Chesapeake.	4
Melongena, cf. subcoronata, Heil- prin, 10 Fulgur [Fulgur], 11	с	* *	c				Pleiocene.	5
Fulgur, cf. spiniger, var. nodulatum, Conrad, 12 Latirus, 13	*	*		*				6
Nassa, 74		*						
Typhis acuticostata, Conrad, 15		*					Chesapeake. Claiborne.	2
Typhis gracilis, Conrad, 16 Scala [Apalia], 17		*					Giaroor lie.	1
Turritella gatunensis, Conrad, 18 Turritella, cf. acropora, Dall, 19	*	* *	*	*	*		Miocene. Recent.	4 4
Turritella. cf. terebriformis (Conrad), Dall, 20 Solarium, cf. bellastriatum, var.	а	*	*	×	*	*	Miocene.	
Vicksburgense, Dall, 21 Crucibulum auricula. var. imbrica-		*	*				Vicksburg.	4
tum. Sowerby, 22		*						
Caliptræa centralis, Conrad	*	* *					Chesapeake.	3
Crepidula fornicata, Lamarck, 23 Natica [Cryptonatica] floridana, Dall Chlorostoma [Omphalius] exoletum,		*	а	*		. а	Chipola.	4
Conrad, 24		*					Chesapeake.	4
Fissuridea, cf. Griscomi. Conrad, 25		*					Older Maryland.	
Helix, cf. adamnis, Dall, 26 Bulimulus ? 27		*		1			Chipola.	4
Balanus		*						
		·	·					1

List of publications: 1. Lea. Isaac, Contributions to Geology. 2. Conrad, T. A., Fossils of the Tertiary Formations. 3. Tuomey and Holmes, Pleiocene Fossils of South Carolina. 4. Dall, W. H., Contributions to the Tertiary Fauna of Florida. 4. Heilprin, Angelo, Explorations on the West Coast of Florida. 6. Whitfield, R. P., Gasteropods of New Jersey, Monograph, U. S. G. S., 18. ,

While there have been already some very valuable results attained in the study of the paleontological remains of certain localities in the Gulf Miocene, chiefly due to the energy of Mr. W. H. Dall, the examination of the geology can hardly be said to have more than begun; and the present paper is offered only as one among pioneers in this direction. A list of the fossils of the Gasteropod Gully locality and of the exposures of the same horizon within a radius of two miles towards the east and southeast are here appended. Owing to the lack of opportunity for the present to complete their study by a comparison with the original types scattered in various museums, the publications used in their identification are indicated in the last column. and the appended remarks will sufficiently describe the particular forms discovered. The main value of this list however, consists in the comparison of the Gasteropod Gully specimens as types, with the corresponding or nearly related species found elsewhere in the Appalachicola embayment, and actually in the writer's possession. a denotes a moderate variation from the forms typical of the Gasteropod Gully Chipola; b denotes distinct variations, therefrom, and c suggests only a similar general habitus and form.

### Notes on the preceding species.

1. The Chattahoochee, Alum Bluff and Bailey's Ferry specimens are decidedly of the Ostrea divaricata type, but from Gasterpod Gully only the free valve is known. 2. The three striæ along the back of the ribs are not so strong as is indicated in Conrad's figure; the Chattahoochee specimens reach only foursevenths of the normal size and have 16 or 17 ribs. 3. Posterior ribs strongest; umbonial ridge very strongly defined posteriorly near the beak; a depressed area or groove anterior to the same near the margin, anteriorly to which with a concavely sinuous outline the breadth of the valves is diminished. 4. Anterior half strongly depressed; ribs (19 or 20) and interspaces about equal; cross striations strong and tuberculate over the anterior ribs, squamose towards the umbonial slope, and coarsely striate posteriorly; a narrow plication follows the posterior hinge line, succeeded below by a broad plication, then two narrow ones, then a broad one, after which the broader plications of the umbonial slope come in. 5. Not exceeding  $45^{mm}$  in length; with elevated concentric ridges about 2<sup>mm</sup> apart, or less regularly arranged. 6. The Chattahoochee specimens are typical, the Gasteropod Gully one is relatively broader, and those from Alum Bluff are 7. In Chattahoochee specimens 4 to 5 revolving smaller. striae ornament the whorls of the spiral. 8. Nucleus unknown; remainder 21.5<sup>mm</sup> long, with 7 whorls, the earlier ones more rapidly tapering, the last 7.7<sup>mm</sup> in diameter, with 9 ribs. 9. Form of the spire and of the posterior end of the aperture between M. ballista, Dall and M. bella, Conrad; outline of the

anterior regions nearer M. bella; length 12.5<sup>mm</sup>. 10. Spines of the shoulder usually 9, reaching 13 on a whorl, variable from short and blunt to larger and more acute, but not normally so acute or with such sharp lateral edges as in the type of M. subcoronata; the area between the angle of the shoulder and the suture is more inclined. 11. Maximum length 37mm, suture just beneath the angle of the shoulder of the preceding whorl, area anterior to the suture gently concave and then rounding into the body, the earlier whorls may be distinctly nodulose, but the nodules usually become obsolete in the last whorl. Spiral striæ present below the body, at times also visible above the rounded angle of the shoulder. The smaller shells with obsolete nodules have the general appearance of Bulbifusus. In the Chattahoochee occurs a species 45<sup>nm</sup> long, with acute spines along the shoulder, 9 or more on a whorl. 12. Spire very low, whorls keeled, suture applied on or just beneath the keel, shoulder flattish, slightly concave, keel strongly angulate, nodulose, or wavy or the last whorl without distinct tuberculation; length 28<sup>mm</sup>. 13. Canal in mature specimens strongly constricted at junction with aperture, more open in immature ones; liræ 6 to 7; plications 2, oftener obsolete; varices narrow, varying to more acute, the alternate ones almost wing-like, resembling Triton. 14. Near Nassa trivittata, Say, with about 15 ribs, crossed by coarse striations which are distinct below, obsolete on the body, and which give rise to a single series of course nodules just below the suture. 15. Spire a little less elevated. 16. Length 18<sup>mm</sup>, width 10<sup>mm</sup>; spire more rapidly tapering, varices 4, triangularly pointed but hardly spinous above, ridges running thence to the sutures above and below, and to the preceding tube. The intermediate tubes in our specimens rise so moderately above the angle of the shoulder as hardly to be more than apertures, not elongated tubes; this may be due to wear. 17. Length 17<sup>mm</sup>, width 6<sup>mm</sup>, 7 or 8 whorls below the nucleus, 12 strong<sup>\*</sup> ribs below, strongest posteriorly, crossed by five distinct striae between the sutures. 18. Varying towards subgrundifera, Dall, with which it is connected by intermediate forms. 19. A distinct large quite rapidly tapering species, with a strong basal (anterior) and an almost equal strong medial, rounded spiral rib, the intermediate portions strongly constricted, the whole ornamented by fine close spiral striae. 20. Very variable. 21. A fine striation between the peripheral keel and the spiral above, as well as below; in addition to the last there are below, first a narrower spiral, then four of nearly equal size, and finally the abruptly broader umbilical carina. 22. Low narrow spirally radiating ribs, becoming obsolete towards the apex, curving towards the right below, crossed obliquely by close distinct radiating striae. 23. A small form. 24. Diameter 8.5mm, spire lower, upper surface more flattened, producing a less regularly rounded periphery. 25. Length 16.8mm, width 1.2<sup>mm</sup>, height 10<sup>mm</sup>, with about 70 radiating striae at the

periphery, the striae being distant at the apex, becoming broader and close at the periphery. These are crossed by concentric striae which are about equally distant towards the apex, but close at the periphery; the result is a cancellated appearance towards the apex which disappears towards the base. 26. Diameter  $7 \cdot 3^{\text{mm}}$ , elevation  $3 \cdot 9^{\text{mm}}$ , spire very low, whorls 5, umbilicus small, open. The outer and inner lips seem to be joined over the body by a V-shaped lamina, of which all of the lower but only a portion of the upper part is preserved in the specimen. 27. Only the five upper whorls are preserved.

### ART. XXXVIII.—Mineralogical Notes; by W. E. HIDDEN.

### Transparent Xenotime, from Alexander County, North Carolina.

AT a locality about one mile southeast of Sulphur Springs, an outcropping of quartz was investigated and a "pocket" of beautiful crystals was opened up. As there was much muscovite associated with the quartz crystals, and in a very disintegrated condition, the whole vein matter was hauled to water and washed after the manner of gold washing, that is to say, in a "rocker." The final concentrates proved to be rich in brilliantly clear monazite and to contain a few small crystals of clear, bright xenotime. The best of these, which were unfortunately the very smallest, were sent to Prof. Penfield for careful measurement of their angles. He states his results as follows : The xenotime crystals gave very good inflections but showed some variation in angles. The best crystal gave the following :

	North Carolina. " Measured.	Dana's 6th Edition. Calculated.
$z \land z'', z \land z',$	$\begin{array}{c} 111 \\ 111 \\ 111 \\ 111 \\ 111 \\ 111 \\ 55 \end{array} \begin{array}{c} 18' \\ 26\frac{1}{2} \end{array}$	82° 22' 55 30

He also measured  $z \land z'' = 82^{\circ} 19'$  and  $82^{\circ} 21\frac{1}{2}'$  on two other crystals.

It is thus seen that the measurements of these new crystals do not vary essentially from those of vom Rath and Klein quoted by Dana. They present the prism m, 110, in combination with the pyramid z, 111, and a steeper pyramid which is probably u, 331; like figures 3 and 4 on p. 483 of Dana's Mineralogy, sixth edition. The color of the crystals was clear yellow-brown. The largest one was only  $3 \times 11$  mm., while those measured were only about  $1 \times 2$  mm. A distinctly twisted gyroidal-like development was positively noticed in the larger crystals. It was impossible to obtain enough of these rare crystals for even an approximate analysis.

### Jurosite, from the Jarilla Mts., Doña Ana Co., New Mexico.

On the "Shoo-ah-me" (the Peublo Indian name for turquois) Mining Claim, situated in the Silver Hills District in the above described region, there are several outcrops of limonite, which at no great depths, change to pyritiferous copper ore. At one of these the crystals of jarosite here referred to, were found in comparative abundance though small and unsatisfactory. Prof. Pentield kindly tested some of them and found them to contain  $Fe_2O_3$ ,  $SO_3$ ,  $H_2O$  and  $K_2O$ , but none were found smooth enough for measurments. The forms presented were apparently c, 0001; r, 1011 and s, 0221. They occur as druses of bright brown crystals having curved faces. It is interesting to add that a fine quality of turquois was being mined less than three rods from where the jarosite was found.

### Green Xenotime, from the Brindletown Gold district of Burke County, North Carolina.

This variety of xenotime occurs as a rare constituent of the auriferous gravels of the region named. It has not as yet been found there *in situ*. The common condition is that of opaque rough crystals, having quite perfect prismatic cleavage, of a gray-brown color and a low degree of hardness. Rarely, the crystals exceed a gram in weight and exceptionally some of quite perfect form over two centimeters in diameter have been found. Even larger groupings, of a polysynthetic character, have been found near the head of Brindle Creek on the land belonging to J. C. Mills just opposite Pilot Mountain.

It was in the interior of some of the larger crystals that the new green variety was found. From its irregular position, within the brown opaque crystals, it seems evident that the green portion represents the original condition and the brown is an alteration product, due to hydration, oxidation, etc. The new material, which is of a bottle-green shade, is transparent to translucent and has a bright vitreous luster. When finely pulverized *it is soluble in hot hydrochloric acid*, which feature is new to the species. It goes readily into solution (excepting the SiO<sub>2</sub>) when boiled with concentrated sulphuric acid in platinum and to the resulting paste sufficient water is added.

Through the kindness of Prof. F. W. Clarke, of the U. S. Geol. Survey, I am enabled to add here analyses by Mr. L. G. Eakins, of both the green xenotime and of the brown alteration product. In conjunction with these an analysis by Blomstrand of a similar xenotime found at Narestö in Norway\* is added for sake of comparison.

\* See Dana's System Min, 6th edition, p. 749.

No. 1. Green.	No. 2. Brown.	No. 3. Narestö.
Eakins.	Eakins.	Blomstrand.
SiO <sub>2</sub> 3.46	3.56	2.36
$ZrO_{2}^{2}$ 1.95	2.19	1.11
UO <sup>*</sup> <sub>2</sub>	1.73	
UO <sub>3</sub> <sup>*</sup>		3.48
$\operatorname{SnO}_2$		0.08
$\mathrm{ThO}_{2}$ tr.	tr.	2.43
PbO <sup>*</sup>		0.68
MgO		0.26
$AJ_2O_3 \dots 0.77$	1.57	0.28
Fe <sup>2</sup> O <sup>3</sup> 0.65	2.79	2.01
Ce O		0.96
(La, Ďi) <sub>2</sub> O <sub>3</sub> 0.93	0.77	
VO )	FF. 40%	30.23
$Er_{2}O_{3} \dots \{ 56.81^{*} \}$	55.43*	24.34
CaO 0.21	0.19	1.09
$P_{2}O_{5}$	29.78	29.23
$\mathbf{F}^{2}$	0.26	
H <sub>2</sub> O 0.57	1.49	1.77
99.85	100.06	100.31
Less O for F	0.23	
	99.83	
	0000	
Sp. grav = $4.68$	4.46	4.49
at 24.2° C.	at 24·4° C.	

The material analyzed by Eakins in both instances, was selected with great care by the use of a lens and was *apparently* more uniform in quality than the analyses would seem to indicate. It is a matter of surprise that the analyses, especially that of the green variety, show so complex a mixture. Calculation shows that, the molecular ratios of the  $P_2O_5$ :  $(Y, Er)_2O_5$ group is as  $21\cdot34: 21\cdot85$  and we therefore must conclude that the SiO<sub>2</sub> is present, not as admixed quartz, but as an essential acidic element in combination with the other constituents : the  $P_2O_5$  being alone *insufficient* for even the  $(Y, Er)_2O_5$  group.

The analysis of the green material may prove a composition due to a partial alteration in the nature of pseudomorphism by gradual substitution, but it seems probable that xenotime<sup>+</sup> is either in truth, at times, a silico-phosphate, like some monazite and auerlite; or it is often mechanically mixed with some

<sup>\*</sup> The Y Er group includes any scandium present and in both cases has a molecular weight = 260 (Eakins).

<sup>&</sup>lt;sup>†</sup> Prof. Penfield has lately shown by his analysis of a Colorado xenotime, found *in situ*, that it does sometimes occur in nature in a condition of almost normal purity. See vol. xlv, p. 398, May, 1893.

cyrtolite (in infinitely fine crystals) and also other silicates of the rare earths. The UO<sub>2</sub> found by Eakins, like the UO<sub>3</sub> found by Blomstrand in the Narestö xenotime, is probably to be regarded as an isomorphous replacement of thoria. The green color would seem to indicate that the UO, was present as a phosphate. The ThO, is not constant even in the same locality, for some of the common xenotime from this same region, tested for thoria alone proved to contain over four per cent.\* Another trial on new material gave 2.36 per cent The fluorine, it will be noticed, is *richest* in the ThO<sub>o</sub>. brown variety (only a mere trace in the green) which is also the most hydrated and richest also in alumina and ferric iron. Prof. Henry A. Rowland, of the Johns Hopkins University, examined spectrographically some of this Brindletown xenotime, several years ago, and reported it to be uncommonly rich in scandium; even more so than the South Carolina polycrase.

### ART. XXXIX.—Conditions of Appalachian Faulting; by BAILEY WILLIS and C. WILLARD HAYES, Appalachian Division U. S. Geological Survey.

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CHAMBERLIN in 1882 suggested that folding and faulting of strata in narrow zones of great sedimentation might be due to the mechanical condition produced in deeply buried layers, which would be bent initially beneath the mass laid upon them before compression produced greater deformation.+ Geologists of the Appalachian division of the U.S. Geological Survey, approaching the problems of structural geology through field study in the belt from Pennsylvania to Alabama and experiments on stratified blocks, which were compressed under shot, were led independently to the conclusion that the condition which determined folding and faulting resided in the strata folded or faulted and was a mechanical condition determined by the frangibility, flexibility or plasticity of the strata and by their attitude as struts toward pressure. The experimental work and some observed facts bearing on the conclusions are described in an article now in press, t and

\* As the thoria was separated by repeated hyposulphite treatments in a neutral HCl solution and precipitated finally as oxalate and as the ignited oxide was pure white, there can be no doubt of its identity.

+ Geology of Wisconsin, vol. 1, p. 76. Mechanics of Appalachian Structure, Bailey Willis, XIIIth Ann. Report U. S. G. S.

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the conditions which gave rise to the great system of overthrusts in the Appalachian province are there discussed.

But the article by Dr. E. A. Smith in this Journal for April, 1893, on Underthrust Folds and Faults, suggests the desirability of briefly presenting our views through the same medium. If the normal Appalachian overthrusts and the socalled "underthrusts" are produced by the same mechanical forces slightly modified by local conditions it seems unnecessary as well as undesirable to create a new species for the latter in the systematic classification of Appalachian structural forms.

First will be stated the antecedent conditions for the development of Appalachian structure; second, the mechanics of stepfolds and thrust-faults and repeated parallel folds or faults; third, application of the theoretical conclusions will be made to the actually observed Appalachian structure, and finally the direction from which the compressing force acted will be briefly discussed.

Sedimentation and initial dips.—The source of the greater part of Paleozoic sediments of the central and southern Appa lachians is generally assumed to be a continental area lying east and southeast of the interior area of deposition. This was doubtless the original source of the material but the later formations are probably largely made up of re-deposited material eroded from those earlier formed. From the observed processes of sedimentation it is known that mechanical sediment from the land is deposited over a zone parallel to the shore and extending to a greater or less distance out to sea. But under the usual conditions of tides and undertow the greatest thickness of the deposit will be in a narrow belt along shore and will gradually lessen seaward. Throughout great masses of sediment it is frequently observed that the layers bear the rippled marked surfaces formed in shallow water, compelling the conclusion that subsidence went on at a rate equal to that of deposition. The subsidence is an argument for isostatic adjustment to shifting load. It is also an argument, on the assumption of a general cause of subsidence other than isostasy, that the effects of such cause may be localized and the subsidence accelerated by loading. Or it might be argued that any force acting vertically may deepen the water and that off shore currents expanding in deeper water and therefore slowing there would deposit heavily upon the subsiding area. Whatever view be taken of the process the fact remains that subsidence has frequently gone on at a rate approximately equal to that of accumulation of strata. The cross section of such a deposit is that of a bi-convex lens. One edge rests against the shore from which it thickens rapidly and then thins gradually seaward. The lower surface of this lens is

the conformable contact between the newer and older strata and it follows that the older strata dip more or less steeply from the shoreward side to the thickest part of the lense and thence rise more gradually seaward. The condition then existing is represented in fig. 1, and the broad shallow trough formed by the deeper strata may be called an original syncline.

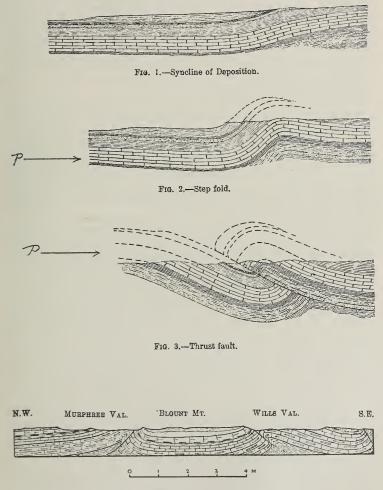


FIG. 4.-Section in Northern Alabama.

That such original synclines of deposition existed in the paleozoic strata of the Appalachians previous to compression is clearly shown from a consideration of the variations in thickness of strata deposited on the great limestone. Thus in Lycoming county, Pennsylvania, the total thickness of strata between the coal measures, XIII, and the Cambro-Silurian limestone is 9700 feet, while in Carbon county it is 23,700 feet. There can be no doubt that the surface on which the coal beds formed was essentially horizontal and it follows that to accommodate this greater thickness beneath a horizontal datum and above the great limestone the latter must have had an *initial dip* from Lycoming to Carbon county. This dip amounted to about 200 feet per mile and carried the limestone down 14,000 feet lower in the Anthracite region than in the Alleghany region. It was a dip due to vertical subsidence, not to compression, and formed the northwestern gentle slope of an original syncline of deposition.

The stratigraphic sections published by the Second Geological Survey of Pennsylvania when compared in detail indicate that each of the anthracite basins is related to an area of maximum deposition in consequence of which the deeper strata assumed the form of an original syncline which later become a syncline of compression. Thus in the Wyoming basin No. XI has a thickness of 150 to 400 feet along the sides but is 1200 feet thick at Shickshinny on the synclinal axis.

In East Tennessee similar original synclines of deposition have been observed, as that in the Bays Mountains where the Silurian shales increase in thickness from 1800 feet on the western side to 4000 or more near the axis, necessitating a very considerable initial dip. Another is represented in fig. 1, p. 259, in which the thicknesses are those observed in a section through Clinch Mountain near Rogersville, Tennessee, but the position of the shore line and the shoreward thinning of the upper strata are hypothetical. In northwest Georgia the increase in thickness by 2000 feet or more in the lower Carboniferous must have produced an original syncline in the present Armuchee basin. Also on the western side of Murphree Valley in Alabama the Lookout sandstone forming the base of the Coal measures is only about 60 feet thick while 15 miles eastward it has a thickness of from 600 to 800 feet, indicating a sharp syncline of deposition on the line of the present Blount Mountain syncline. The effect of this initial eastward dip upon the structure will be indicated later.

The original synclines so far mentioned have axes parallel with the general trend of the present axes of compression which they doubtless determined, but in northern Georgia and Alabama there is evidence of an old shore line extending nearly east and west with the accompanying syncline of deposition parallel to it on the north. This has doubtless been the chief factor in producing many of the peculiar structural features which characterize this region.\*

Considered with reference to their massiveness, strata in the Appalachian province fall into three great groups: at the base a series of thinly stratified Cambrian sandstones, shales and limestones; in the middle a very massive Cambro-Silurian limestone, and on top a series of thinly stratified sandstones and shales. Locally, strata in the upper and lower series become massive but none have the extent, uniformity and massiveness of the great limestone, which is 2500 to 6000 feet thick in the folded zone and covers more than 600,000 square miles. On any line across the zone of deformation this stratum would most efficiently transmit a pressure acting tangentially to the earth's surface, and if before compression it were anywhere bent upward or downward, then during compression the preëxisting bend would determine the point at which it would yield to sufficient force ; it would act as a crooked strut.

That such bends did exist in the great limestone, before the action of compression which produced the Appalachian folds, has been shown from a consideration of the process of sedimentation and from the observed synclines of deposition mentioned above. In the Appalachian province in such original synclines the steeper seaward dip was northwestward and the gentler shoreward dip was southeastward. Now if strata occupying the initial position represented in fig. 1, p. 259, be subjected to a sufficient compressive force they will yield at the bends; the original anticline, and the original syncline will be exaggerated while the steeper and hence shorter limb of the syncline will occupy the position of an arm between the forces of a couple. It will therefore be rotated so that the original seaward dip will grow steeper and, if compression continues long enough, may be overturned. Such a fold may be compared to a step of broad tread and moderate rise and hence may be called a *stepfold*, fig. 2, p. 259. This has long been recognized as the usual antecedent of an Appalachian thrust-fault.

Development of Thrust faults.—There are three mechanical conditions by either one of which a thrust-fault may develop from a stepfold. The pressure tending to exaggerate the fold will be most efficiently transmitted by the most massive stratum, in the Appalachians by the great Silurian limestone, and any condition which weakens this stratum may lead to a fault.

The first condition is erosion. The development of folds is probably gradual, and although the original position may be submarine the rise of an anticline will eventually lift its crest

\* The Overthrust Faults of the Southern Appalachians, C. W. Hayes; Bull. Geol. Soc. Am., vol. ii, pp. 141-152.

above the not very deep waters along shore. From the beginning of emergence the arch will be subject to degradation and its waste will be deposited in the adjacent synclines. Then, the crown of the arch being removed, the separated limbs of any rigid stratum will tend to approach if compression continues. If the stratum dips steeply the horizontal component of this movement will be small and the vertical component will be masked by erosion; but if the dip be gentle the rigid stratum, to which no resistance save friction is opposed, may advance over the eroded surface and a thrust-fault be developed on a horizontal or gently dipping plane. Such a thrust-fault might readily escape observation if one end of the rigid stratum were pushed upon the other or might be mistaken for an unconformity by deposition if it were exposed at the contact of younger with older strata.

The second condition, which may lead to the development of a thrust-fault from a stepfold, is fracture. If a rigid stratum be sufficiently bent, in the absence of a load adequate to cause continued flexure, the stratum will break and the crack will offer a plane of weakness on which a thrust-fault may occur. Fig. 3, p. 259. The crack will be radial to the curve and the fault being determined by the resistance offered by the gently dipping limb of the adjacent anticline. will usually have a fault-dip parallel to the dip of that limb. This is the common type of Appalachian thrust-faults. The essential condition, that the rigid stratum should be free from excessive load, may arise either because the deposits over that stratum were never very thick or because erosion cuts away overlying strata on the crown of the arch and thus removes the load. The great Silurian limestone in the Appalachian district of thrust-faults bore from 2500 to 10,000 feet of strata; and in the district of folding without the development of faults it bore from 10,000 to 30,000 feet of strata. To depths of five miles in the earth the pressure due to gravity is approximately proportioned to the depth and one foot of strata corresponds to about  $1\frac{1}{8}$  pounds of pressure per square inch. Hence we infer that the great limestone broke and thrust-faults were produced under loads of 2800 to 11,000 pounds per square inch, but it folded without breaking under loads of 11,000 to 34,000 pounds per square inch.

The third condition, under which a thrust-fault may develop from a stepfold is that of plastic flow. A sufficiently loaded stratum may be stretched in its overturned limb and so thinned or torn apart as to constitute an overthrust. This type can develop only under excessive load. It is not known in the Appalachians except in the case of coal beds of the Anthracite region and has been most fully described by Heim from examples observed in the Alps.

This explanation of the origin of stepfolds rests upon conditions of sedimentation along shore and may suffice for those cases in which the observed facts of stratigraphy indicate the antecedent development of a syncline of deposition. But geologists familiar with the number and relations of Appalachian folds and thrust faults may fairly object to the assumption of a shore line and an original syncline for each one. A supplementary explanation is required and it must account for the extraordinary parallelism generally existing among the axes. This explanation may be found in the results of the development of competent anticlines.

Competent structure.—When a force tangential to the earth's surface affects a stratified mass, it is transmitted by the strata in the direction of their lateral extent and by each stratum according to its rigidity. To illustrate, if pressure be applied to the side of a pile of tissue paper in which are leaves of card board of the same size, the predominant effective pressure apparent on the other side is that transmitted by the cardboards. The stratum which thus most effectively transmits pressure may be called the competent stratum; and it is plain that the term "competent" is significant of relative rigidity, not of an absolute quality. In the Appalachian province *the* competent stratum was the great limestone.

If the pressure transmitted by a competent stratum arrives at a bend due to initial dip, the force is resolved into two components; the one acts in the direction of the stratification, the other acts in a line normal to the stratum, or radially. If the curve be convex upward it will develop into an anticline of deformation when the radial component of the force is strong enough to bend the strata and carry up the superincumbent load. The strength of this component is determined by the strength of the original force and by the initial curvature of the stratum. No anticline can develop unless the radial component of the force for a given original curvature is equal to the task, nor for a given force unless the original curvature is sufficient to deflect a competent component. If these conditions be fulfilled the competent stratum will rise in anticlinal form and will carry the overlying load on its crown. The zone beneath the crown is then relieved of load, which is transferred to the limbs.\*

If the stratified series be made up of many beds of nearly equal competency alternating with relatively incompetent beds such as thin interbedded limestones and shales, then each com-

\* H. Schardt, Pull. de la Société Vaudoise des Sci. Nat., vol. xx, 1884. pp. 143-146. B. Willis, Mechanics of App. Structure, XIIIth Ann. Rep. U. S. G. S.

petent layer will carry up the immediately overlying incompetent layer and the total weight raised in the anticline upon its numerous competent arches will be distributed through their limbs to many points of support. But if the stratified series consists of one massive competent stratum overlaid by a great thickness of relatively incompetent strata, then the total weight raised on the anticline will be transferred by the massive competent stratum to those parts of the curve which are concave upward, that is to the adjacent synclines. Applying these general conclusions to the special case of an original Appalachian stepfold we may represent (fig. 5) the competent



FIG. 5.-Development of original competent anticline A.

stratum by a single heavy black line. If the weight raised by the competent anticline A be W, then the limbs of the arch will transmit the weights w' and w'' whose sum will be equal to W and whose ratio will depend on the relative dips of the two limbs. As the limb A S becomes steeper w' will increase in proportion to w'' and its effect will be concentrated at the foot of A S. If the arch A be eroded such part of the sediment as falls in the syncline S will also concentrate in a narrow zone, while that which falls on the other limb will be distributed on its gentle slope. The downward pressure thus produced beneath the original syncline S, is directly related to W; it is an indeterminate weight which may be designated x(fig. 6).



FIG. 6.-Development of consequent competent anticline A'.

The weight x tends to depress the limb SA' and if it causes depression at S it must displace the subjacent support, which will move toward A, the region of relief; the limb S A' of the competent stratum will then sink downward in a long gentle curve. x must be greater than the weight required to displace the support at S and the excess will be exerted in bending S A'; being effective at a point A' so far distant from S that the moment of x into S A' is greater than the resistance which the competent stratum opposes to bending.

Now the force of compression, P, is resolved at A' into two sets of components, those tangential and those radial to the curve. As the curvature increases through the effect of the moment  $x \times S$  A', the radial components increase in proportion to the tangential and when their upward directed force exceeds the weight on the competent stratum at A', a competent anticline will develop there.

The anticline A' is subsequent in time and causally related to the anticline A. A' is therefore a consequent to A and may be called a *consequent fold* in distinction from A, the original fold. The distance of A' from A is determined by the length of the limb SA', which is itself determined by conditions in the strata; therefore so long as the stratigraphic series remains invariable the distance A' A will be constant and the two folds will be parallel. This is the condition which any explanation of Appalachian folding must satisfy.

The form of the anticline A' will probably vary in different cases: it may be symmetrical or unsymmetrical, and if the latter, it may be overthrown to one side or the other. With a steep initial dip from A' toward S, there might be developed an overturned limb facing the original fold (fig. 7) and then, if both the original and the consequent folds were faulted the thrust-faults would present opposite fault-dips. This however



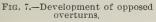


FIG. 8.—Development of parallel overturns.

is the rare exception and the reason for the overturn of the consequent in the same direction as the original fold appears from a further analysis of the process. The form of the gently sloping arm of the syncline S A' is determined largely by the depression of S and is slightly convex upward from A' to a point of inflexion, i, near S, (fig. 6). Now the force P is continuously resolved upon the curve A' i into components acting tangentially along the stratification and radially at right angles to the same. The tangential components are opposed by the resistance at S while the radial components tend to lift the curved limb A' i against the weight of the overlying strata and the resistance to bending. In the flat lying strata on the other side of A' the force P is not resolved into components so that the only force tending to elevate this part of the competent stratum is the radial component at A'. This elevation is opposed by the weight of the superincumbent load and the

resistance to bending offered by the strata, both of which forces tend to hold down this portion of the competent stratum. But the radial components directed upward in the convex curve at and near A' must carry up the crown of the arch, if it develops as a competent structure, and in so doing they cause the beginning of a concave curve in the section PA'. As this curve becomes sharper, the force P is resolved into components tangential and radial to the curve, the latter being directed downward. Thus the limb S' A', fig. 8, occupies a position between forces acting downward at one end and upward at the other and a neutral point n becomes a center of rotation for that limb. Moreover the force P is absorbed in the development of these radial components and with increasing curvature there is decreasing pressure in the other limb A'S and consequently less and less tendency to further bending. The flow of material from the point of support S' of the competent arch toward the zone of relief A' beneath the arch also tends to promote the rotation of A' S'. Thus a consequent stepfold is developed parallel to and overturned in the same direction as the original fold which depended upon initial dips. The same process may continue with the formation of an indefinite number of parallel folds all turned in the same direction and each consequent upon the one next preceding it in time and position.

Another factor in determining the direction of overturn of the consequent fold, as pointed out by Dutton,\* may be deep seated isostatic flow. If such flow of material from the area of sedimentation toward the area of erosion actually takes place its effect may be to displace S and S', the supports of the anticlinal arches, toward the shore line and so to add to the rotation of the seaward limbs of the anticlines.

Next to the parallelism and continuity of their axes the most remarkable feature of the Appalachian folds is the uniformity in the direction of their steeper sides. This indicates a corresponding uniformity in the initial dips of the synclines of deposition which determined the form of the original stepfolds. It also indicates the prevalence of conditions favorable for the westward overturn of the consequent folds. As shown in the above analysis of the process by which the consequent folds are formed, an important condition is the long western limb of the original syncline convex upward and with gentle dip eastward.

Two exceptions to this westward inclination of the folds are known in the southern part of the province. These are the northern portions of the Wills Valley and Murphree Valley

\* On some of the greater problems of Physical Geology, C. E. Dutton, Bull. Phil. Soc. Washington, vol. xi, 1889, p. 60. anticlines The former is overturned eastward and the latter is overturned and faulted, the plane of the thrust-fault dipping steeply toward the west. The latter case is the one mentioned by Dr. Smith as illustrating his type of so-called "underthrust faults." The structure is shown in the sections accompanying the Gadsden Atlas Sheet.\*

Comparing the thickness of the Carboniferous formations of this region we are able to reconstruct the original syncline of deposition which has determined the location and form of the Murphree Valley fold. In other parts of this region there is a very gradual westward thinning observable in all the Paleozoic formations implying, if any, very moderate eastward initial dips. In this particular locality, however, the Lookout sandstone, the lower portion of the coal measures, has its maximum thickness of 800 feet in the Blount Mountain syncline; from this it thins rapidly westward to 60 feet or less west of the Murphree Valley anticline and also eastward, though less rapidly to Chandler Mountain. Hence there must have been an original syncline of deposition whose axis coincided with the Blount Mountain syncline and which had initial dips eastward steeper than those westward. These initial eastward dips were sufficiently pronounced to produce an overturn toward the southeast. The form of the fold naturally determined the dip of the thrust-fault when faulting was developed as a secondary effect of continued compression.

Since the Murphree Valley fold shows a further stage of development than the southern portion of the Wills Valley fold it may perhaps properly be regarded as an original stepfold developed on the westward side of the syncline of deposition while the latter is the consequent fold.

The reason for the eastward overturn in the second case mentioned, the northern end of Wills Valley, is more obscure than in the case of Murphree Valley. The form of the fold is shown on the Stevenson Sheet † It is quite possible that the coal measures thicken eastward from Fox Mountain toward the Lookout Mountain syncline, indicating an initial eastward dip sufficient to determine the direction of overturn of the resulting fold. Whatever may have been the cause of the abnormal form which the fold assumed it was purely local, for the fold becomes symmetrical a few miles from its northern end and thence southward assumes the normal form with overturn toward the west.

Direction of the compressing force.—Thus far the origin and direction of a force adequate to produce folding and fault-

<sup>\*</sup> Geologic Atlas of the United States, Gadsden Folio, Geology by C. W. Hayes. In press.

 $<sup>\</sup>ensuremath{\stackrel{+}{_{\!\!\!\!\!\!}}}$  Geologic Atlas of the United States, Stevenson Folio, Geology by C. W. Hayes. In press.

ing have not been considered in presenting the mechanics of the problems; although it is too large a subject for full discussion here it cannot be altogether omitted. It has long been assumed that the force in the Appalachian province came from the southeast, because the folds are overthrown toward the northwest. Heim disposed of this argument in pointing out that the overturn must always be toward the deeper syncline; and it is here shown that, in accordance with the conditions of deposition, the deeper syncline in original folds must be off the land. Therefore the direction of the force cannot be inferred from the direction of the overturn.

Force and resistance must be equal or movement ensues. Acting against flat strata, a sufficient pressure must be opposed by a sufficiently resistant buttress or the strata must move forward. A continental mass of crystalline rocks might constitute such a buttress and flat strata pressed against it might remain in static equilibrium so long as pressure and resistance were not strong enough to crush them. If the pressure were a growing one and the resisting buttress were firmer than the strata, then they must eventually yield either by crushing or Observation shows that the latter is the common bending. result and the lines of flexure are determined by preëxisting deflections from a horizontal attitude. When anticlines begin to develop as competent structures the force is exerted against the load upon the rising arch and the resistance is correspondingly diminished. Hence it follows that strata between a growing force and a resistant mass are subjected uniformly if at all to compression which is equal in opposite directions. Therefore, in the Appalachians the compressing force was directed both northwestward and southeastward. But from the time folding begins there will be movement from the force toward the resistance. This movement we conceive to have been in the Appalachians a superficial flow of a broad zone from northwest to southeast, from the sea toward the land. In the development of thrust-faults the *relative* movement at the surface was determined by the direction of fault-dips which depended in turn upon the direction of overturn in the original and consequent stepfolds; these are generally overturned to the northwest, and the apparent direction of the pressure is thus the opposite of the real direction. If we consider the mass above a thrust fault as stationary, the faults are all underthrusts; or if we consider the motion with reference to the mass below the fault plane, they are all overthrusts.

# ART. XL. - On the Double Halides of Antimony with Rubidium; by H. L. WHEELER

THE investigations of the double halides of antimony and rubidium have hitherto been confined to the chlorides, and the following salts have been described :

1:1	Rubidium	Antimony	Chloride,	RbCl.SbCl.
5:3	"	"	"	$5 \mathrm{RbCl}$ . $3 \mathrm{SbCl}$
23:10	66	66	66	23RbCl.10SbCl
6:1	"	66	66	6RbCl.SbCl

The first three of these compounds were described by Remsen and Saunders.\* These investigators, after a careful study of the subject came to the conclusion that the salt 6RbCl. SbCl. described by Godeffroy<sup>+</sup> does not exist.

It has been shown by the author of the present article that the 3:2 type of double salts is probably the only one formed by the combination of the arsenic halides with those of cæsium and rubidium.<sup>‡</sup> Moreover, since this type was observed by Schæffer§ in the case of the double halides of antimony with sodium, potassium, and ammonium, and, since Remsen and Saunders obtained the salt 3CsCl. 2SbCl, it seemed probable that this type of double halides would exist with rubidium and antimony. A thorough re-examination of the chlorides has therefore been undertaken and the investigation has been extended to the bromides and iodides. As a result of this investigation the following compounds have been obtained :

RbCl. 2SbCl. H.O RbCl. SbCl<sub>3</sub>. 3RbCl.2SbCl3. 3RbBr. 2SbBr, 3RbI.2SbI. 23RbCl. 10SbCl, (?) 23RbBr. 10SbBr, (?)

The first chloride. RbCl. 2SbCl<sub>3</sub>. H<sub>2</sub>O, is a new type of antimony rubidium halides, which Remsen and Saunders did not obtain. The second, 1:1, confirms the results of these investigators, while the series of 3:2 salts, which includes a chloride, bromide, and iodide, corresponds to the type expected from analogy. The difference between the percentage composition required for the 3:2 chloride and that required for the 5:3 formula of Remsen and Saunders is small, and it is to be noticed that these authors do not consider their formula as definitely established. They say, "The analytical results obtained from different samples varied considerably and it does

\* Am. Chem. Jour., xiv, 155. ‡ This Journal, 111, xlvi, 88.

+ Berichte, viii, 9. § Pogg. Ann., cix, 611. not appear possible to obtain the salt in pure condition." It will be noticed that most of the analyses of the 3:2 chloride, made in the present investigation, show a composition intermediate between what is required for the formulas of the 3:2 and the 5:3 salts, but the bromide and the iodide were readily obtained in pure condition and gave analytical results closely corresponding to the 3:2 formula. Moreover the chloride, bromide and iodide just mentioned are all hexagonal and may be referred to axes which correspond closely to those of the 3:2 arsenic compounds. The chloride and bromide with a complex composition (23:10?) confirm the results of Remsen and Saunders on the chloride. The formula suggested by them has been retained, subject to uncertainty. It will be seen beyond that, as Remsen and Saunders have noticed, the ratio 16:7 corresponds very closely to the analyses, and it may be added that the ratios 9:4 and 7:3 differ so little from the other two that it would be very difficult to distinguish between any of these ratios by analysis.

For the preparation of the double halides the constituents were mixed in the presence of the corresponding dilute acids. In the case of the chlorides a 10 per cent acid was used. The mixtures were then evaporated until crystals separated on cooling. Further details will be given with the descriptions of the salts. In the case of each salt several crops were prepared and analyzed, and an attempt has been made to determine approximately the limits of the conditions under which these double halides are formed. It may be added that the analytical results are not selected, for with the exception of two antimony determinations, where an error had been detected, every determination that was made has been given.

## Method of Analysis.

The salts were removed from the mother liquor, and, after pressing on smooth filter paper, were dried in the air for a short time. Portions of a little less than one-half a gram were taken for analysis. In order to determine the halogens, silver nitrate was added to a solution of the substance in water containing a little tartaric and nitric acids, the mixture was then warmed on the water bath for a couple of hours and finally, after standing twelve hours, the silver halide was collected, ignited and weighed in a Gooch crucible in the usual manner. The determination of the antimony and rubidium was effected in a separate sample. In order to do this, the salts were dissolved in a little dilute hydrochloric acid and the solutions were diluted with boiling water. Hydrogen sulphide was then used to precipitate the antimony and, when the solutions had cooled, the resulting sulphide was filtered on asbestos in a Gooch crucible, washed with water and alcohol and then heated to  $230^{\circ}$  in an oven filled with carbonic acid. On cooling, the sulphide was weighed as  $\text{Sb}_2\text{S}_3$ . The rubidium was determined by evaporating the filtrate from the antimony sulphide to dryness with an excess of sulphuric acid, the residue was then converted into normal sulphate by ignition in a stream of air containing ammonia. The atomic weights used in the calculation of results were the following :

## Cl, 35.5; Br, 80; I, 127; Sb, 120; Rb, 85.5

## The Double Chlorides.

The crystals of the double chlorides are colorless, with the exception of the salt 3RbCl. 2SbCl<sub>s</sub>; this salt has a pale yellow color exactly similar to the salts 3RbCl. 2AsCl<sub>s</sub> and 3CsCl. 2AsCl<sub>s</sub>. The stability of the double chlorides, on exposure, appears to vary inversely with the quantity of antimony chloride which they contain.

1:2 Rubidium Antimony Chloride,  $RbCl. 2SbCl_s. H_gO.$ —This new salt was obtained from hydrochloric acid solution when the constituents were mixed in the proportion of ten, eight or six molecules of SbCl, to one of RbCl. On concentrating these mixtures supersaturated solutions were obtained which sometimes remained for days without giving crystals, but on shaking or stirring with a glass rod the crystallization was induced. The crystals separate in the form of elongated, colorless, monoclinic tables. Analysis of different crops gave :

	From	solutions	of	From solution of 8SbCl <sub>3</sub> to	From solution of 6SbCl <sub>3</sub>	Calculated for
	10SbCl <sub>3</sub> to 1RbCl.			1RbCl.	to 1 RbCl.	RbCl. 2SbCl3. H2O.
Rb	14.61	14.71	14.74	14.64	15.07	14.44
$\mathbf{Sb}$	40.75	40.97	41.09	41.07	40.97	40.54
Cl	41.83	41.53	41.11			41.98
$H_{2}O$	3.20	3.10	3.18	3.08		3.04

The crystals of this salt have a brilliant luster when first removed from the mother liquor, but on exposure they soon lose their luster, becoming opaque and decomposing. In the preparation of this salt for analysis the crystals were crushed and thoroughly pressed on filter paper, and when it was certain that the powder did not contain any mechanically mixed water, it was placed in a weighing tube. This salt is readily distinguished from the other colorless double halides of rubidium and antimony by the fact that it melts at 77°.

1:1 Rubidium Antimony Chloride,  $RbCl. SbCl_{s}$  — This salt was first described by Remsen and Saunders;\* they say that "if the excess of antimony chloride . . . be very great, a colorless salt crystallizing in elongated, apparently orthorhombic, crystals is obtained." I have found that by mixing the constituents in hydrochloric acid solutions, in the proportion of four or three molecules of SbCl<sub>s</sub> to one of RbCl, crystals of similar appearance were obtained. The solutions require a considerable degree of concentration and the mother liquor is more or less syrupy, hence the rubidium determinations came low and the antimony high. Analysis gave :

From solution of 4SbCl <sub>3</sub> to 1B	on From solution RbCl. of 3SbCl <sub>3</sub> to 1RbCl.	Calculated for RbCl.SbCl <sub>s</sub> .
Rb 23.67	23.96	24.61
Sb 35.38	34.99	34.53
Cl 40.70	40.73	40.86

A solution of antimony and rubidium chloride in the proportion of 2½ molecules of the former to one of the latter gave a mixture of this salt and the yellow one described below. As has been observed by Remsen and Saunders, crystals of this salt rapidly lose their luster on exposure. They give no definite melting point below the temperature of boiling sulphuric acid.

3:2 Rubidium Antimony Chloride, 3 Rb Cl. 2 Sb Cl. - This is the salt to which Remsen and Saunders assign the formula 5RbCl.3SbCl<sub>s</sub>. They obtained this compound on adding "a considerable excess " of antimony chloride to a solution of the salt 23RbCl. 10SbCl<sub>a</sub>. They describe the crystals as sometimes resembling a rhombohedron in general shape and having a pale yellow color, and they remark that "this is noteworthy, because the more complex salt (23RbCl. 10SbCl.) and the simpler one (RbCl. SbCl<sub>s</sub>) are both colorless. It is to be remembered, however, that the salt Cs<sub>3</sub>Sb<sub>2</sub>Cl<sub>2</sub> (3CsCl. 2SbCl<sub>3</sub>) is also yellow." It may be added that both 3OsCl. 2AsCl, and 3RbCl. 2AsCl, are pale yellow. Remsen and Saunders also remark "As the formula of this rubidium salt is not very simple, and as the substance could not be recrystallized, on account of the strong tendency towards the formation of the very complex salt, the formula suggested below can hardly be considered as definitely established."

\* Loc. cit.

I have found that when solutions of antimony chloride and rubidium chloride are mixed in the proportion of one and onefifth molecules of the former to one molecule of the latter a pale yellow-salt is obtained crystallizing in rhombohedrons. In one case on obtaining a crop of crystals from a solution of 2SbCl, to 1RbCl, in strong HCl, the yellow rhombohedrons were seen to be mixed with the colorless hexagonal plates, presumably of the salt 23RbCl. 10SbCl,? It was also found that a wide difference exists in the solubility of these two salts in warm solutions, the yellow crystals dissolved with difficulty, while on the other hand, the salt 23:10 went into solution with only a slight elevation of temperature. If the crystals of the yellow salt are warmed in the mother liquor they become opaque throughout without losing their pale yellow color. It seems probable that impurities are dissolved out by this operation and that no decomposition takes place, for the decomposition products and the other double chlorides are colorless. An analysis of a crop obtained in this manner corresponded very closely to the formula 3RbCl. 2SbCl. Analysis gave:

	Fr solutio 2SbC 1Rb	l <sub>3</sub> to	soluti 1 <del>1</del> 51	om ons of oCl <sub>3</sub> to bCl.	From solutions of 2SbCl <sub>3</sub> to 1RbCl heated.	Calculated for 3RbCl. 2SbCl <sub>s</sub> .	Calculated for 5RbCl. 3SbCl <sub>2</sub> .
Rb Sb Cl	28.68	32·19 28·67 38·42	33•34 28•55 38•32	$31.86 \\ 28.46$	$31.30 \\ 29.44 \\ 38.98$	31·44 29·41 39·15	33·28 28·03 38·69

23:10? Rubidium Antimony Chloride,  $23 Rb Cl. 10 Sb Cl_{a}$ . —For the preparation of this compound, a sample of rubidium chloride was used which had been specially purified for the purpose by the method recently described by Professor H. L. Wells\* of this laboratory. The purification of this sample was repeated after the product failed to give spectroscopic reactions for potassium and cæsium.

If solutions of antimony and rubidium chlorides are mixed in the proportion of one molecule of SbCl, to one, four or six molecules of RbCl, the crystals obtained are the "colorless six-sided plates, tables, or thicker crystals," to which Remsen and Saunders have assigned the formula 23RbCl. 10SbCl<sub>3</sub>. The average results of the analyses of the different crops of the double chloride gave figures closely agreeing with those of the above authors, but the ratio of rubidium to antimony came somewhat lower than theirs. Analysis gave :

## \* This Journal, III, xlvi, 188.

AM. JOUR. SCI.—THIRD SERIES, VOL. XLVI, NO. 274.—OCTOBER, 1893.

	From solut 6RbC 1Sb(	ion I to	From solution 4RbCl to 1SbCl <sub>3</sub> .	From solution 1RbCl to 1SbCl <sub>3</sub> .	Sample recrystal- lized from 10 % HCl.	Average	e. Ratio.
Rb	38.98	38.55	38.83	38.62	38.60	38.71	6 2.28
$\mathbf{Sb}$	23.76		23.98	23.52	23.81	23.76	7 1.00
Cl	37.16	36.97			36.95	37.02	6 5.26
	23 Rb	Calculated 3RbCl.10 38.90 23.7	SbCl₃. 161 <b>3</b>	Calc. for RbCl , 7SbCl <sub>3</sub> . 38.85 23.86	Calc. fo 9RbCl.43 38*57 24*06	SbCl₃. 7 7	Calc. for RbCl. 3SbCl <sub>3</sub> . 39.21 23.58
	Cl	37.21	7	37.29	37.37	7	37.21

It is to be noticed that this salt is formed under conditions varying more widely than in the case of any of the other double rubidium antimony chlorides. It can be exposed to the air for several days without losing its luster; on long exposure it becomes covered with a white, opaque layer, probably of antimony oxychloride.

## The Double Bromides.

The bromides were obtained in the form of brilliant yellow, six-sided plates, resembling the double arsenic bromides of rubidium and cæsium. They are comparatively stable in the air, but on long exposure the crystals lose their luster.

3:2 Rubidium Antimony Bromide,  $3RbBr. 2SbBr_{3}$ .—This salt was obtained from dilute hydrobromic acid solutions when the constituents were mixed in the proportion of two and three-tenths and also four molecules of RbBr to one of SbBr<sub>3</sub>, it was also the only one formed when antimony bromide was present in the solutions in excess. It will be seen that a much larger range of conditions exists for the preparation of the salt 3RbBr. 2SbBr<sub>3</sub> than in the case of the corresponding double chloride. Moreover, the bromide can be recrystallized unaltered from dilute hydrobromic acid.

Analysis gave:

		n solution aining a		From solution	From solution 4RbBr	Sample of latter recrystal-	Calculated for
	large	excess o	I	23RbBr.	to 1	lized from	3RbBr.
-		SbBr₃.		to 10SbBrs.	SbBr <sub>3</sub> .	HBr.	2SbBr₃.
$\mathbf{Rb}$	21.55	21.18	20.96	21.16	21.53	20.92	21.08
$\mathbf{Sb}$		20.07	20.13	19.98	19.59	19.91	19.73
Br	59.30	•				59.07	59.19

23: 10 (?) Rubidium Antimony Bromide, 23 RbBr. 108bBr. —This salt was obtained when dilute hydrobromic acid solutions of rubidium and antimony bromides were mixed in the proportion of six, eight and thirteen molecules of the former to one of the latter. The crystals obtained on slowly cooling these mixtures, with the exception of their strong yellow color, closely resemble the corresponding complex chloride. If the solutions are rapidly cooled the salt separates in the form of brilliant spangles. The average of the following results gives a remarkably close ratio to that required for the formula 23 RbBr.  $108 \text{bBr}_s$ .

Analysis gave :

	From solution 6RbBr to	From solution 8RbBr to		m solution		Sample of latter recrystallized from
DI	1SbBr <sub>3</sub> .	1SbBr <sub>3</sub> .		Br to 1Sbl		conc. HBr.
Rb	26.66	26.16	26.92	26.60	26.71	26.39
$\mathbf{Sb}$	16.11	16.23	16.18	16.26	16.22	16.18
$\operatorname{Br}$			57.27	57.23		57.41
	Calculated f RbBr.10Sb		ulated for Br. 7SbBr <sub>3</sub> .	Calcula 9RbBr.		Calculated for $7 \text{RbBr} \cdot 3 \text{SbBr}_3$ .
. RI	0 26.	55	26.47	26	27	26.74
$\mathbf{Sb}$	16	20	16.25	16	.38	16.08
Br	57	25	57.28	57	•35	57.18
Average of analytical results. ————————————————————————————————————						
Rh	26.57	· <b>3</b> 107	or 23.	03 or 16	3·12 or	9·21 or 6·90
Sb		·1349			.00 "	4.00 " 3.00
			10 0	50 1	00	100 000
Br	57.30	$\cdot 7162$	" 53.	09 " 37	7.16 "	21.23 " 15.92

It is to be noticed that this salt is formed within a much smaller range of conditions than in the case of the chloride and can only be recrystallized from strong hydrobromic acid solutions. When recrystallized from moderately strong acid a mixture of the salts 23:10 and 3:2 was obtained, but from dilute acid a pure crop of the 3:2 compound separated.

Recrystallized from strong HBr.	Recrystallized from dilute HBr.	Calculated for 3RbBr.2SbBr <sub>3</sub> .
Rb 25.54	21.89	21.08
Sb 16.93	19.70	19.73
Br 57.77		59.19

# The Double Iodide.

3:2 Rubidium Antimony Iodide, 3RbI.2SbI,.—The formation of this salt was observed when a solution of rubidium iodide in hydriodic acid was saturated hot with antimony iodide, it was also obtained from a solution of antimony iodide in a large excess of rubidium iodide. The best crystals are obtained when a considerable quantity of antimony iodide is present; under these conditions large deep red lozenge shaped crystals separate. Analysis gave:

Large excess	Large excess	Calculated for
of RbI.	of SbI <sub>3</sub> .	$3 RbI . 2 SbI_3.$
Rb 16.28	14.82	15.64
Sb 14.14	15.17	14.64
I 69.76	69.55	69.72

On exposure to the air the crystals slowly lose their luster.

## Crystallography.

The crystallization of the 3:2 double salts is hexagonal. In general the habit is rhombohedral and they can all be referred to axes of nearly equal length. The double bromide and iodide have a perfect basal cleavage, like the salts of the arsenic series, while the chloride gave only a conchoidal fracture. The axial ratios of the salts is shown by the following table, the ratios of the corresponding arsenic salts being given for comparison.

From this table it may be seen that the substitution of arsenic by antimony produces little if any effect in the lengths of the axes, and, in each series the vertical axes lengthen as the atomic weight of the halogen increases.

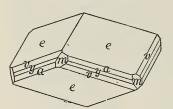


Fig. 1.

 $3RbCl. 2SbCl_{3}$ .—This salt unlike the others of the series, shows rhombohedral tetartohedrism. In one crop, where the crystals measured 5 to 7<sup>mm</sup> in diameter, the faces were developed on every crystal as in fig. 1, the forms being

a, 11 $\overline{2}0$ , *i*-2 *e*, 01 $\overline{1}2$ ,  $-\frac{1}{2}$  *y*,  $\overline{2}532$ ,  $-\frac{1}{2}^5 r$  *m*, 10 $\overline{1}0$ , I *v*,  $\overline{1}3\overline{2}2$ ,  $-\frac{1}{2}$ ,  $^3r$ 

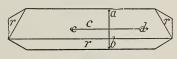
On a second crop only e and a were developed.

	Measured.	Calculated.
e ~ e. 0112 ~ 1102	56° 18'	
e ~ v, 0112 ~ 1322	29 53	29° 55'
$e \land y, \ \bar{1}3\bar{2}2 \land \bar{2}5\bar{3}2$	11 29	11 26
$y \land a, \ \bar{2}5\bar{3}2 \land \bar{1}2\bar{1}0$	20 29	20 29

This salt differs from all the others of the series, since, it is the only one on which tetartohedrism has been observed. Whether the others are really tetartohedral, but have not shown it owing to the absence of highly modified forms, cannot be told at present. Also the basal cleavage, which is so prominent on all of the others, could not be detected, while the one half rhombohedron e was only observed on this salt. A basal section was prepared, which in convergent polarized light showed a normal, uniaxial interference figure, the double refraction being negative, like the corresponding arsenic compound.

 $3RbBr . 2SbBr_s.$  — Crystals of this salt were prepared up to 7<sup>mm</sup> in diameter. The habit is generally that of six-sided plates, fig. 2, having the forms c, 0001, O; r,  $10\bar{1}1$ , 1 and z,  $01\bar{1}1$ , -1. In one crop c, r and m were developed with some of the rhombohedral faces predominating to such an extent that the crystals looked like prisms, represented in basal projection by fig. 3.





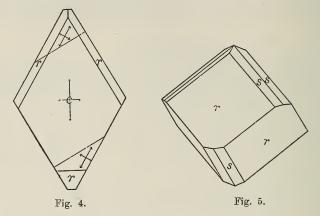
	Measured.	Calculated.
$r \land c, 10\overline{1}1 \land 0001$	*52° 21′	
$r \land z$ , $10\overline{1}1 \land 01\overline{1}1$	48° 0	47° 57'

None of the crystals show normal optical properties. Crystals like fig. 3 showed for the most part an extinction parallel to the direction c-d, sometimes with twinned lamellæ prominent at one end. In convergent polarized light no interference figure was observed normal to c but some of the crystals like fig. 3 could be tilted up on a rhombohedron face and showed an acute bisectrix nearly normal to r. The axial angle was small and the dispersion strong, the optical axes being in the plane a-b for green and normal to that for red light, the interference figure looking like that of brookite.

 $3RbI.2SbI_{s}$ .—This salt unlike the corresponding arsenic compound was obtained in crystals of considerable size some over  $10^{\text{mm}}$  in diameter. When prepared with an excess of SbI<sub>s</sub> usually lozenge-shaped crystals were obtained shown in basal projection in fig. 4. These were often grouped in twin position, penetration twins being prominent with a rhombohedron as twinning plane. From solutions containing an excess of RbI, the rhombohedral habit was observed, sometimes with a negative scalenohedron  $\& 18\cdot9\cdot17, -\frac{7}{17}-\frac{9}{7}$ , bevelling its pole edges, fig. 5.

			Measu	ired.	Calcul	ated.
$m \wedge r$ ,	$10\bar{1}0$	∧ 10Ī1	*35°	° 6′		
$r \land c,$	$10\bar{1}1$	~ 0001	54	43	48°	18'
		$^{0111}$	47	15	48	18
		<u>∧</u> 1101	89	50	90	14
s ~ s,	$18\bar{9}17$	<u>∧ 19817</u>	6	40	6	21

The basal cleavage was prominent and sections parallel to this showed abnormal optical properties. Thin plates from the crystals like fig. 4 showed middle and end sections with



extinctions in the directions indicated by the arrows. In convergent light no interference figure was observed. This salt then like 3RbBr. 2SbBr, and 3RbI. 2AsI, is only pseudo-hexagonal being abnormal in its optical properties.

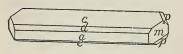


Fig. 6.

RbCl. SbCl. - The crystallization of this salt is monoclinic. Crystals were obtained 10mm The forms observed long. were

a,	100,	$i$ - $\overline{i}$	
c.	001.	0	

The habit is shown in fig. 6. The axial ratio is  $\dot{a}:b:c'=$  $1.732:1.000:1.085; \beta = 0.01 \land 100 = 65^{\circ} 34'.$ 

	Measured.	Calculated.
$a \sim c$ , $100 \sim 001$	*65° 34'	
$a \land m, 100 \land 110$	*57 37	
$c \land e, 001 \land \overline{1}01$	*37 36	
$m \land m, 110 \land \bar{1}10$	64 46	64° 46'
$a' \land e, \overline{100} \land \overline{101}$	76 54	76 50
$p \land e, \bar{1}\bar{1}1 \land \bar{1}01$	46 28	46 23
$p  c,  \bar{1}\bar{1}1  c001$	·56 50	56 52
$c \wedge d, 001 \wedge 101$	24 21	24 22
$d \land a, 101 \land 100$	41 24	41 12

In polarized light these crystals show an extinction parallel to the ortho-axis. With crystals flattened parallel to the basal plane an obtuse bisectrix may be seen nearly normal to the base. The plane of the optical axis being at right angles to the symmetry plane.

 $RbCl. 2SbCl_{3}. H_{2}O.$ —The crystallization of this salt is monoclinic. Crystals were made up to a length of about 9 or  $10^{\text{mm}}$ . The forms observed were:

α,	100,	i-ī						
с,	001,	0	d,	021,	2-ì	p,	$\frac{221}{101}$ ,	2
m,	110,	1	е,	011,	1- <i>ì</i>	x,	101,	1-ī

The habit is shown in fig. 7. The axial ratio is  $\dot{a}: b: \dot{c} = 1.699$ : 1:0.820  $\beta = 0.01 \times 100.89^{\circ} 28\frac{1}{2}'$ .

_	Measured.	Calculated.
$m \land m, 110 \land \overline{1}10$	*60° 57′	
$a \land x, 100 \land \overline{1}01$	64 49	$64^{\circ} \ 40'$
$m \land a, 110 \land 100$	59 32	59 32
$a \land c, 100 \land 001$	*89 283	
$x \land c, \bar{1}01 \land 001$	$*25 51\frac{1}{5}$	
c ~ e, 001 ~ 011	39 10	39 21
$c \land d, 001 \land 021$	58 20	58 37
$a \land p, 100 \land 221$	63 5	63 6
$p \land d, 221 \land 021$	27 - 5	26 37

The crystals flattened parallel to the ortho pinacoid, show in polarized light an extinction parallel to the ortho-axis and in convergent light a bisectrix and one of the ring systems appear near the limits of the field. The plane of the optical axis is the clino pinacoid.

The 23:10 bromide is pseudo-hexagonal. Basal plates always showed an intricate twinning when examined in polarized light. The pyramidal faces were horizontally striated and to such an extent that no satisfactory measurements could be made. In every respect this compound resembles the 23:10 chloride described by Remsen and Saunders.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the present investigation and to Prof. S. L. Penfield under whose generous supervision the crystallography of these salts was investigated.

Sheffield Scientific School, June, 1893.

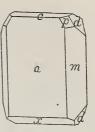


Fig. 7.

# ART. XLI.—On the Separation of Copper from Cadmium by the Iodide Method; by PHILIP E BROWNING.

[Contributions from the Kent Chemical Laboratory of Yale College-XXVIII.]

THE separation of copper from cadmium by the precipitation of the cuprous iodide by appropriate means has long been known. Pisani\* mentions the fact that potassium iodide can be used to effect precipitations and claims that a satisfactory separation can be made in this way. Flajolot states that potassium iodide cannot be used as a precipitant on account of the solubility of cuprous iodide in that reagent, nor can hydriodic acid be employed if nitric acid is present. He recommends that the solution containing copper be brought to acidity with sulphuric acid, that a considerable excess of sulphurous acid be added and that the precipitation be effected by hydriodic acid. Under this treatment he finds that only an unweighable or at least a very small trace of copper remains dissolved. Kohnert in a paper of more recent date, in which he reviews the various methods for the separation of copper from cadmium, states that the iodide method is impracticable on account of the solubility of cuprous iodide both in excess of hydriodic acid and in potassium iodide.

The work to be described was undertaken to determine if possible under what conditions the method may be safely used. Solutions of copper and cadmium sulphates were made and standardized by treating definite portions, measured from burettes and weighed, by appropriate means, the average of closely agreeing results being taken as the standard. A solution of potassium iodide of approximately ten per cent strength, was used throughout the work. The amount of the copper solution generally taken (25 cm<sup>3</sup>) contained about 0.12 grm. of copper and the potassium iodide necessary to completely precipitate the iodide was about 0.6 grm. or 6 cm<sup>3</sup> of the solution. I have in no case used less than 10 cm<sup>3</sup> or 1 grm. of the iodide. In experiments (1) and (2) the free iodine separating on the addition of the potassium iodide was bleached with sulphurous acid and the cuprous iodide filtered off immediately. In experiment (3) no sulphurous acid was added but the solution was boiled until a considerable amount of the free iodine was expelled. In experiment (4) the boiling to expel the free iodine completely was necessarily carried on until the solution was evaporated nearly to dryness. Experiments (5) to (14) were

<sup>\*</sup> Compt. rend.. xlvii, 294.

<sup>&</sup>lt;sup>†</sup> Journ. f. prakt. Chem, lxi, 105.

Zeitschr. Anal. Chem., xxvii, p. 203. Jour. Anal. Chem., vol. iii, p. 339.

made to show the effect of varying amounts of potassium iodide, and were all conducted in the same manner, the standard copper solution being measured from a burette into a counterpoised beaker and weighed, the potassium iodide in solution added, the whole evaporated to dryness to insure the expulsion of the iodine, and water added to the amount indicated in the table. The filtration was made under gentle pressure, by means of a Bunsen filtering flask, on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. It is advisable to use a moderately thick felt and not to allow the felt to run dry nor to remove the pressure during the filtration, on account of the tendency of the cuprous iodide to pull through under these conditions. The precipitate was washed thoroughly with either hot or cold water, the washings never amounting to less than 100 cm<sup>3</sup>. The crucible containing the cuprous iodide was placed in an air bath and the precipitate dried at a temperature between 120° C. and 150° C., and weighed. The first weight was uniformly constant. It would seem from experiments (4) to (12) that a moderate excess of potassium iodide has no great solvent effect upon the precipitated cuprous iodide, while free iodine and large amounts of hydriodic acid have a decided solvent effect as shown in experiments (1), (2), (3). In two cases where 1 grm. and 2 grm. respectively of potassium iodide were used to precipitate about 0.12 grm. of copper the filtrate from the first gave no reaction with either ammonia or acetic acid and potassium ferrocyanide, and the second gave no reaction with ammonia and with potassium ferrocyanide only a trace.

These filtrates before testing for copper were treated with potassium nitrite and sulphuric acid to remove the iodide and

	Series I.*							
		Copper found	Error in		Final volume			
Cop	per taken.	(weighed as $Cu_2I_2$ ).	Copper.	KI used.	of liquid.			
	grm.	grm.	grm.	grm.	$\mathrm{cm}^{\overline{3}}$ .			
(1)	0.1189	0.1093	0.0096-	1	300			
(2)	0.1197	$0\ 1050$	0.0147 -	6.6	6.6			
(3)	0.1191	0.1026	0.0135-	6 6	64			
(4)	0.1194	0.1189	0.0002 -	6 6	66			
(5)	0.1194	0.1196	0.0002 +	6.6	100			
(6)	0.1191	0.1194	0.0003 +	6.6	4.6			
(7)	0.1193	0.1193	0.0000	2	6.6			
(8)	0.0049	0.0045	0.0004-	6 6	5.6			
(9)	0.0021	0.0042	0.0004-	<b>6 6</b>	4.4			
(10)	0.1192	0.1192	0.0000	3	6.6			
(11)	0.1192	0.1188	0.0004 -	4	44			
(12)	0.1191	0.1189	0.0002 -	6.6	200			
(13)	0.1193	0.1182	0.0011	5	"			
(14)	0.1193	0.1179	0 0014-	66	64			

\* The copper is calculated as the metal in this table.

oxidize the copper. I have no doubt that when the potassium iodide is in excess some copper goes into solution, but the amount is very small unless the excess of iodide is very great. I may add here that when the potassium iodide is in very large excess the mixture of potassium iodide and cuprous iodide melts as the solution becomes concentrated by evaporation and a solution is obtained having a deep iodine color. This color does not disappear on further evaporation and the result obtained upon filtering the cuprous iodide after dilution with water invariably shows considerable loss. In the event of noticing the phenomenon mentioned it is best to throw aside the determination before completion and start another using less of the iodide.

The separation of the copper from the cadmium was taken up next. Definite portions of the cadmium solution were measured into the same beakers with the copper solution and weighed, and enough potassium iodide was added to precipitate the whole as cuprous iodide if no cadmium were present. The solution was evaporated to dryness to remove iodine and diluted to the amount stated in the table. The precipitated cuprous iodide was filtered upon an asbestos felt, thoroughly washed, dried and weighed as before described. The filtrate and washings contained, of course, the cadmium together with the excess of potassium iodide and potassium sulphate formed in the reaction, and the determination of the cadmium was not as simple a matter as might at first be supposed. In the presence of potassium iodide, hydrogen sulphide did not give a precipitate in acid or neutral solution which could be filtered. After removing the potassium iodide, however, by treating with sulphuric acid and potassium nitrite, it was found to be possible to precipitate all the cadmium as sulphide, but in such form that filtration was extremely slow, which was peculiarly disadvantageous in this case inasmuch as the presence of the large amount of alkaline salts present made prolonged washing of the sulphide necessary. Ammonium sulphide gave better results, the precipitate falling in good form even in the presence of potassium iodide, but here also the slow filtration was a disadvantage. I have had recourse therefore to the method of precipitating by sodium carbonate and weighing as oxide. This method has generally been regarded as inaccurate, but my experience has shown that it is one of the best of the processes employed for the estimation of cadmium when the filtrations and ignitions are made upon asbestos. Two determinations of the cadmium alone gave results agreeing closely with the standard determinations made by evaporating definite portions of the solution of the sulphate to dryness and igniting at low redness and weighing as the anhydrous sulphate.

The filtrate containing the cadmium was heated to boiling and sufficient sodium carbonate added to complete the precipitation. On further boiling the precipitate became granular and filtered easily. The precipitate was washed with hot water several times by decantation, the washings being passed through the felt to prevent loss of any of the precipitate. Washing was continued until the filtrate gave no reactions for either sulphate or iodide. The crucible containing the carbonate was heated gently at first, then gradually to a higher degree until the lower half of the crucible was red and the white carbonate had changed to the brown oxide. This heating was repeated until a constant weight was obtained. In some of the separations the faintest suspicion of a blue color in the carbonate suggested the presence of the fraction of a milligram of copper which probably escaped the separation process.

				SERIES	11.			
4		Copper			Cadmium			
		found	Error		found	Error		Found
	Copper	(weighed as	s on	Cadmium	(weighed	on	ΚI	volume
	taken.	$Cu_2I_2$ ).	Copper.	taken.	as CdO.)	cadmium.	used.	of liquid.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	$\mathrm{cm}^{3}$ .
(1)	0.2383	0.2386	0.0003 +	0.0484	0.0490	0.0006 +	2	100
(2)	0.1192	0.1182	0.0007-	0.2439	0.2430	0.0001 +	44	**
(3)	0.1193	0.1194	0.0001 +	0.1942	0.1942	0.0000	"	"
(4)	0.1188	0.1190	0.0002 +	0.2422	0.2421	0.0001 -	"	200
(5)	0.1201	0.1201	0.0000	0.2426	0.2428	0.0002 +	44	100
(6)	0.1193	0.1193	0.0000	0.2436	0.5433	0.0003 -	44	68
(7)	0.0239	0.0238	0.0001-	0.1934	0.1932	0.0002-	1	6.6
(8)	0.0236	0.0239	0.0003 +	0.1942	0.1936	0.0006-	66	4.6
(9)	0.0239	0.0343	0.0003 +	0.1444	0.1442	0.0002-	66	**
(10)	0.0538	0.0238	0.0000	0.1467	0.1461	0.0006-	٤،	""

The method is simple in manipulation and the results are fairly accurate.

# ART. XLII.—A New Meteorite from Hamblen County, Tennessee; by L. G. EAKINS.

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

Professor Safford at once took steps to secure these pieces, and visited the locality where they were found. Here he succeeded in finding a few more fragments, which had the appearance of having been buried in the soil and afterward turned up by the plow. These various pieces now in Professor Safford's possession have a total weight of about 36 pounds, two of them weighing respectively 11 pounds and 13 pounds. A specimen sent by Professor Safford to the U.S. National Museum, and now in its collection, furnished the material for this investigation.

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

The analysis was made in the usual way for this class of meteorites; that is, by separating the metallic and siliceous portions, both by picking and by the magnet, and analyzing separately the nickeliferous iron, the silicates soluble in hydrochloric acid and those insoluble. The metallic and siliceous portions of this meteorite are, approximately, equal in amount; the iron being quite malleable and unusually tough.

The analysis is as follows:

Nickellierous Iron.	
Fe	90.92
Ni	7.71
Co	.80
Cu	tr.
Р	
S	.04
_	

Michaliforoug

9	9	•	6	6

#### SILICEOUS PORTION.

	Soluble i	in HCl.	Insc	Insoluble in HCl.		
		Calc. to	Molecular		Calc. to	Molecular
Ana	lysis.	100%	ratios.	Analysis.	100%	ratios.
SiO	16.79	45.61	.760	31.47	50.67	•844
$Al_2O_3$	8.33	22.62	·222	9.25	14.89	•146
$\operatorname{Cr}_{2}O_{3}$				<b>·</b> 82	1.32	•009
FeO	4.88	11.73	.163	6.55	10.55	$\cdot 147$
NiO	•39	1.06	•014			
MnO				•47	•76	•010
CaO	5.19	14.09	·252	2.24	3.61	•064
MgO	1.34	3.64	·091	11.16	17.98	•449
K <sub>0</sub> O				.02	.03	.003
Na <sub>2</sub> O				.12	•19	.003
${\operatorname{P}}_{{}_2}{\operatorname{\acute{O}}}_{{}_5}$	•46	1.25	•009			
$\mathbf{S}^{*}$	•25					
	37.63	100.00		62.10	100.00	

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

In many stony meteorites olivine is a considerable constituent, generally forming the bulk of the soluble silicate; but in this case the analysis shows olivine to be present in but small proportion, if at all. It is interesting to note that both the soluble and insoluble portions have practically the same molecular ratios, the soluble portion reducing itself essentially to RAl<sub>2</sub>SiO<sub>4</sub>, in which R=Ca, Fe; and the insoluble part to the same formula, where R=Mg, Fe; both being equivalent to aluminous enstatite or pyroxene.

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

The other alternative is to assume a complex molecule which is split into two sections by the action of the acid.

The meteorite is now known as the Safford meteorite. Laboratory U. S. Geological Survey.

# ART. XLIII.—On the Ventral Plates of the Carapace of the genus Holonema of Newberry; by HENRY S. WILLIAMS.

IN the summer of 1890 I exhibited photographs of several plates, associated together on a slab of sandstone which I referred to *Holonema*, one of the plates (m. v. of figure beyond) being the same in shape and markings as the original plate described by Claypole as the "ventro-median" or "lozenge-plate" of "Pterichthys," and named by him *Pterichthys rugosa.*\* Messrs. Cope and Claypole both examined my photograph at the time and remarked upon the close resemblance to the arrangement of plates on the back of *Bothriolepis.* In the account given by Claypole in the American geologist,<sup>†</sup> the plates are described as dorsal, and their position is reversed, the plate a.m. v., or anterior median ventral, being called "post-dorso-median," although the general shape of the plates is correct, it having been reproduced, mainly, from a copy of my photograph.<sup>‡</sup>

In the Proceedings of the U. S. National Museum, vol. xiv, p. 256, Cope refers to the same photographs as representing

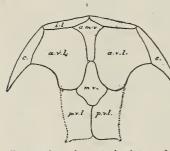
\* Am. Phil. Soc., 1883.

† Vol. vi, p. 255, 1890.

‡ See figure, ibid., page 256.

## 286 H. S. Williams—Ventral Plates of the Holonema.

the posterior part of the carapace, speaking of the plates a. v. l. (fig. 2, beyond) as "posterior lateral" dorsals. My first impression was that the plates were ventral; and in a letter from Dr. Newberry the same interpretation of the plates was made. "I imagine your plates are from the plastron," . . . "there should be two other plates in the plastron overlapping the posterior end" of the plate marked m. v., which he spoke of as the "central plate of the plastron;" and he further said, "your plate A (a. m. v. of fig. 2) is altogether new." With this conflict of opinion and knowing then of no analogous arrangement of plates by which to settle the question, I left the matter for further light. The restoration of the ventral plates of the carapace of *Phlyctænaspis acadica* Whiteaves, by Traquair,\* furnishes the needed clue. Whiteaves had described the dorsal part of the carapace as *Coccosteus acadicus*, and had figured two plates which he referred to the ventral part of the same. His specimens were from the lower Devonian of Cambelltown in Canada, Dr. Traquair on examining specimens from the same locality discovered a large portion of the ventral shield, with nearly all its plates in situ, and



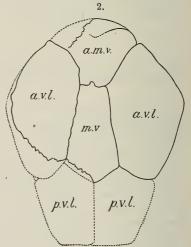
Restoration of ventral plates of *Phlyctenaspis Acadica* Whiteaves, after Traquair. Reduction about  $\frac{1}{2}$ .

Restoration of ventral plates of *Holonema rugosa* Claypole. Reduced to  $\frac{1}{2}$  nat. size.

from it, with the aid of detatched specimens, the restoration was made, of which a copy is given in figure 1. Examination of the restoration and its description shows the probable rela-

\* Geol. Mag., 1893, p. 148.

+ Trans. Roy. Soc. Canada, vol. vi, sect. iv, p. 3. pl. IX, with a woodcut.

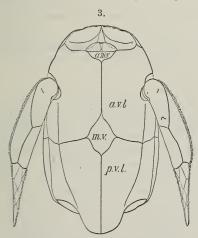


tions of the plates of *Holonema*, as will be seen by comparing figures 1 and 2.\*

The corresponding plates are indicated by the same letters in the two figures: *i. l.*, interlateral, *c.*, cornu or lateral spine, *a. m. v.*, anterior median ventral, *a. v. l.*, anterior ventro-lateral, *m. v.*, median ventral, *p. v. l.*, posterior ventro lateral. The continuous lines indicate outlines that are preserved in the specimens, and the dotted lines, the probable outlines of the perfect plate.

On the specimen from which figure 2 is made there are also traces of impressions of heavy spine-like bones, but their shape is not determined; their presence however is sufficient to indicate that the same animal, of which the plates figured are preserved, possessed also either pectoral limbs or, at least, some more massive bones than the thin, flat plates of which the form is distinctly preserved.

The "pectoral limb," or "pectoral spine" as it is called in the description by Copet (fig. 5), is probably the terminal



4.

Ventral carapace of *Pterichthys* (Bothriolepis) canadensis Whiteaves, after Whiteaves.  $\frac{1}{3}$ . Terminal finger of pectoral limb of *B. canadensis*, nat. size, after Whiteaves. "Pectoral spine of *Holonema* sp." nat. size, after Cope.

5.

\* After handing this paper to the editor I have noticed that Mr. A. Smith Woodward had already pointed out Claypole's error of interpretation, saying "The post-dorso-median" plate of Claypole is obviously the anterior median ventral. while the "post-dorso-lateral" and "dorso-lateral" of the same author are the anterior and "posterior ventro-lateral plates respectively." Catalogue of Fossil Fishes, Brit. Museum, part II, p. 315.

<sup>†</sup>On the pectoral limb of the genus Holonema of Newberry; Proc. U. S. N. Museum, vol. xiv.

part of the pectoral limb of *Bothriolepis canadensis*. The "three elongate narrow hexagons," with "sutures extending from the lateral angles of the hexagons to the border of the spine" described by Cope as characteristic of this spine of *Holonema*, correspond so exactly to the sutures of the terminal finger of the limb of *Bothriolepis canadensis* figured by Whiteaves (figures 3 and 4) as to suggest not only generic but specific identity. From the figure given by Cope, with the interpretation of its relations here given, it may be inferred that there was some motion at the joint between the two parts of the arm. Pander's dissection and description of the arm of *Asterolepis* make the movement to have probably been of no great amount.

It is hoped that other bones or plates may be brought to light illustrating the structure of this interesting genus of fishes. The specimen from which the above restoration was made was found by Prof. C. S. Prosser, near Oxford, N. Y. in the Oneonta sandstone, of the lower part of the Upper Devonian.

ART. XLIV.—On some Minerals from the Manganese Mines of St. Marcel, in Piedmont, Italy; by S. L. PENFIELD.

## Alurgite.

IN 1865 Breithaupt gave a brief description\* of a deep red mica from St. Marcel, to which he gave the name alurgite, from aloupyos, meaning purple. The portion which he at that time had selected for analysis was accidentally lost and since then it seems never to have been investigated. The writer's attention was called to the mineral by Dr. A. E. Foote. of Philadelphia, who sent some of it to New Haven for identification, and a preliminary examination, followed by a chemical analysis and a study of its physical properties have shown that it is a distinct species. Its identity with the alurgite of Breithaupt, was first suggested to the writer by Prof. A. J. Moses of the Columbia School of Mines and has been confirmed by Prof. A. Weisbach of the Bergakademie at Freiberg, to whom specimens were sent and to whom the author's. thanks are due for comparing them with Breithaupt's original specimens.

The crystallization of alurgite is monoclinic; the structure is micaceous and the cleavage basal, though not so perfect as

\* Berg- und hüttenmännische Zeitung, xxiv, p. 336, 1865.

## Manganese mines of St. Marcel, in Italy.

that of muscovite. Cleavage plates are flexible and somewhat elastic. No distinct crystals have been observed but Breithaupt mentions plates with traces of hexagonal outline. The mica occurs as an aggregate of plates, imbedded in a soda rich pyroxene, which will be described later on. The largest cleavage plates that have been observed are about 15mm in diameter. When examined in convergent polarized light some show a uniaxial others a biaxial interference figure, the double refraction being rather strong and negative. Breithaupt mentions a uniaxial interference figure, but in a footnote states that at the same locality a second mica is found, somewhat lighter in color, which is strongly biaxial. The uniaxial character is undoubtedly the result of twinning, for plates can be found, which in some parts are uniaxial, in others biaxial, and where the plane of the optical axes is in two different positions. Some, moreover, give a confused interference figure, as would be expected from two or more biaxial plates, placed one above the other in twin position. There is no difference in specific gravity between the uniaxial and biaxial plates, they are identical in behavior before the blowpipe and there is every reason for believing that they are the same chemical substance. Two measurements were made of the divergence of the optical axes as follows:

# $2E.y. (Na flame) = 57^{\circ} 0' and 56^{\circ} 5'$

The dispersion is distinct,  $\rho > v$ .

When treated with a mixture of strong hydrofluoric and sulphuric acids the biaxial plates show monosymmetric etching figures while those of the uniaxial plates are triangular or hexagonal, similar to those of muscovite and biotite, described by H. Baumhauer.\* The percussion figure is a normal six rayed star. The mica is of the first class according to Tschermak, the plane of the optical axes being at right angles to the symmetry plane, as shown by the etching or the percussion figure. The color will serve as one of the best means of identifying this mica. It is a deep brownish-copper red; the intensity of which in transmitted light, varying of course with the thickness. Cleavage pieces have something the color of clear chips of almandine garnet. The basal cleavage gives a peculiar pearly luster and a sort of coppery metallic tone, like some varieties of red foil. Breithaupt compares the color to lamellar cinnabar and its resemblance to some of the foliated zincite from Franklin, N. J., is very close. The fine powder is pale pink. What is rather remarkable for a colored mica is that its ratio of absorption is so nearly alike in all directions

\* Sitzb. Akad. München, 1874, p. 245 and 1875, p. 99.

AM. JOUR. Sci.—THIRD SERIES, VOL. XLVI, NO. 274.—OCTOBER, 1893. 20 that its pleochroism is not very marked; the axial colors for a and c are red with a purplish cast, for b brownish red.

Before the blowpipe alurgite first swells and then fuses at about 3 to a slightly yellowish, blebby glass and gives a faint potash flame. With sodium carbonate in the oxidizing flame a green bead, Mn, but with borax a violet color is only obtained after adding a large quantity of the mineral, indicating that the amount of manganese is not very great. In the closed tube at high temperature neutral water is given off. The finely powdered mineral is almost absolutely insoluble in boiling concentrated sulphuric or hydrochloric acids. After fusion it is also insoluble. The specific gravity of a number of pieces was taken by means of the heavy solution, and found to be between 2.835 and 2.849. Breithaupt gives 2.984-3.00. The hardness is about 3.

The results of the analysis of the air dry powder are given below under A. Under B we have the same after calculating  $Fe_2O_3$  and  $Mn_2O_3$  as  $Al_2O_3$ , MnO as MgO, Na<sub>2</sub>O as  $K_2O$  and recalculating to 100 per cent.

	А.	В.	Ratio.	
SiO <sub>2</sub>	53.22	53.57	·893	SiO <sub>2</sub>
Al <sub>2</sub> Õ,	21.19	22.68	$\cdot 222$	(AlÔH)O _ ·444
Fe <sub>2</sub> O <sub>3</sub>	1.22			
Mn <sub>2</sub> O <sub>3</sub>	.87			
MnO	·18			
MgO	6.05	6.16	$\cdot 154$	$(MgOH)_2O \cdot 077$
K <sub>2</sub> O	11.20	11.80	$\cdot 125$	$ \begin{array}{c} (MgOH)_{2}O & 077 \\ K_{2}O & 125 \end{array} $
Na <sub>2</sub> O H <sub>2</sub> O	$\cdot 34$			i
H <sub>2</sub> O	5.75	$5.79 \div 9$	$\cdot 643$	H <sub>2</sub> O •022
	99.99	100.00		

The water was determined as loss on ignition, and that it is present in the mineral as hydroxyl is shown by the following fractional determinations :

> Two hours at 100° C. 0.74" " 200 " 0.48" " 300 " 0.17Total..... 1.39 per cent loss.

The iron was found to be all ferric and, moreover, when weighed quantities of the mineral and ferrous sulphate were dissolved together in sulphuric and hydrofluoric acids, and titrated with potassium permanganate, it was found that some of the ferrous sulphate was oxidized by the mineral, which must have resulted from the presence of a higher oxide of manganese. The amount of this oxidation was determined and gave a basis for calculating the per cent of  $Mn_2O_3$ , a blank determination having previously given the triffing amount of oxidation from the air, which was deducted in the calculation. It is probable that the deep red color of the mineral is due to the presence of  $Mn_2O_3$ , for it is well known that the higher oxides of manganese have intense coloring power, while that of MnO is very slight. Thus this mineral with about one per cent of the oxides of manganese has a much deeper color than rhodonite with 50 per cent of MnO.

In calculating the formula it was found that the amount of hydroxyl was a little more than sufficient to unite with the alumina to form the bivalent radical (AlOH) and with the magnesia to form the univalent radical (MgOH). Regarding the (MgOH)<sub>2</sub>O and the slight excess of H<sub>2</sub>O as isomorphous with K<sub>2</sub>O the ratio of the SiO<sub>2</sub>: (AlOH)O: [(MgOH), K, H]<sub>2</sub>  $O = \cdot 893 : \cdot 444 : \cdot 224 = 4 \cdot 0 : 1 \cdot 99 : 1 \cdot 00$  or 4 : 2 : 1. The formula is then R<sub>2</sub>(AlOH)<sub>2</sub>Si<sub>4</sub>O<sub>11</sub> where R equals MgOH, K and very little H, but it seems still better to write this as a metasilicate, HR<sub>2</sub>(AlOH)AlSi<sub>4</sub>O<sub>12</sub>. According to the mica theory of Prof. F. W. Clarke<sup>\*</sup> this composition can also be expressed as a combination of the following molecules in the proportion 1:1

$$\begin{array}{ccc} \mathbf{\sim} \operatorname{Si}_{3} \mathcal{O}_{3} \equiv \mathcal{H}_{3} & \mathbf{\sim} \operatorname{Si}_{0} \equiv \mathcal{R}_{3} \\ \operatorname{Al} - \operatorname{Si}_{3} \mathcal{O}_{3} \equiv \mathcal{R}_{3} & \operatorname{Al} - \operatorname{SiO}_{4} \equiv \left( \operatorname{AlOH} \right)_{3} \\ \mathbf{\sim} \operatorname{Si}_{3} \mathcal{O}_{5} \equiv \operatorname{Al} & \mathbf{\sim} \operatorname{SiO}_{4} \equiv \left( \operatorname{AlOH} \right)_{3} \end{array}$$

Chemically this mica is distinct from any known species. It is more closely related to lepidolite than to any of the others, being similar to it in the  $SiO_2$ .  $Al_2O_3$  and  $K_2O$  percentages. The composition of both can be expressed as metasilicates, they are insoluble in acids and before the blowpipe are easily fusible. Although essentially a potash alumina mica, it differs from muscovite in its high  $SiO_2$  and low  $Al_2O_3$  and in its fusibility, while it is still further removed from biotite and manganophyllite, with which it has been correlated by some authors, by its high silica and insolubility in acids. In a classification, therefore, alurgite should occupy a position near lepidolite and as a distinct species.

## Pyroxene rich in soda, or jadeite.

The alurgite is associated with and imbedded in a soda rich pyroxene. This occurs as an interwoven aggregate of prismatic crystals, resembling in structure a rather coarsely crystallized jadeite. The material is very tough and shows no

\* This Journal, III, xxxviii, p. 384.

The color is a sort of ash gray with a slight crystal faces. reddish tone. Specimens of the gray tephroite associated with the foliated red zincite from Franklin, N. J., bear a most remarkable resemblance to those of this pyroxene with the alurgite. Before the blowpipe it fuses readily to a black bead and imparts a yellow color to the flame. With the fluxes it reacts for iron and manganese. It is insoluble in hydrochloric acid. In thin sections under the microscope the presence of a black ore, piedmontite, alurgite and numerous minute rutile crystals could be detected. The pyroxene showed a prismatic development, a large angle of extinction and a faint though perceptible pleochroism; in clinopinacoid sections for a very pale rose, for c very pale blue. A section across the prism showed the characteristic prismatic cleavage of pyroxene, and in convergent light an optical axis, nearly in the center of the field, the plane of the optical axes being the clinopinacoid. Sections which approximated closely to the orthopinacoid also showed in convergent light an optical axis; all indicating the pyroxene character.

The material for the chemical analysis was crushed and sifted to a uniform grain and separated by means of the barium mercuric iodide solution. The material was not quite uniform in specific gravity, and, therefore, fearing that it might be a mixture, two portions were taken. The one for analysis A varying between 3 382 and 3 338 and for analysis B between 3 338 and 3 257. These portions when examined with the microscope were found to be quite free from impurities, the heavier showing occasional particles of piedmontite and on the whole somewhat clearer grains than those of portion B. The analyses of the two portions are as follows:

	А.	в.	Mean.	Ratio.	CaMg(SiO <sub>3</sub> ) <sub>2</sub> .	NaR(SiO3)2*
$SiO_2$	54.39	54.78	54.59	·910	·264	·646
Al <sub>2</sub> Ó <sub>3</sub>	9.93	9.56	9.74	·095 )		
Fe <sub>2</sub> O <sub>3</sub> -	11.78	12.19	11.99	$\begin{array}{c} \cdot 075 \\ \cdot 075 \\ \cdot 007 \end{array}$		.177
Mn203.	1.21	•92	1.06	·007 )		
MnO	•66	•50	•58	·008 )		
MgO	5.01	5.06	5.03	$(126 \\ (130) $	•264	
CaO	7.29	7.19	7.24	•130)		
Na <sub>2</sub> O _	9.40	9.24	9.32	.150 ) .159		·153
K <sub>2</sub> Ó	•24	•24	•24	$\left. \begin{array}{c} \cdot 150 \\ \cdot 003 \end{array} \right\} \cdot 153$		105
Ign	•38	•35	•37			
-						

## 100.29 100.03 100.16

The two analyses are so nearly alike that they will serve as duplicates, showing that the material was quite pure and homogeneous. In calculating a formula, therefore, the ratio has been derived from the average. It will be seen from the ratio that the MgO and CaO are present in the proportion 1:1 as in normal diopside MgCa(SiO<sub>3</sub>)<sub>2</sub>. Deducting from the total ratio MnO+MgO+CaO:SiO<sub>2</sub> =  $\cdot 264:264 = 1:1$ , there remains SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + Mn<sub>2</sub>O<sub>3</sub>: Na<sub>2</sub>O + K<sub>2</sub>O =  $\cdot 646:$  $\cdot 177: \cdot 153 = 4\cdot00: 1\cdot09: 0\cdot94$  or nearly 4:1:1, which is required by a metasilicate of the general formula NaR(SiO<sub>3</sub>)<sub>2</sub>. The mineral may therefore be considered as containing the following molecular compounds:

Diopside	MgCa(SiO <sub>3</sub> ),	28.8 pe	r cent.
Jadeite	$NaAl(SiO_3)_2^2$	35.7	"
Acmite	NaFe(SiO),	32.5	"
?	NaMn (SiO,),		"
	\$ 37.2		
		100.0	"

These results throw some light on the soda and sesquioxide rich pyroxenes, showing that in this case, at least, they are normal metasilicates. Moreover this mineral holds about the same relation to the pyroxenes that glaucophane does to the amphiboles, being also similar in the orientation of its pleochroism.

As far as can be learned, the pyroxene which agrees most closely with this in composition is a jadeite or chloromelanite from Mexico, analyzed by A. Damour<sup>\*</sup> and containing 8.89 per cent of Fe<sub>2</sub>O<sub>3</sub>, equivalent to 25.7 per cent of the acmite molecule. The color is described as black, in thin section deep green and this is in strong contrast to the Piedmont mineral, which with a larger percentage of Fe<sub>2</sub>O<sub>3</sub> is light in color. It is a well known fact that glasses which are colored green by iron can be decolorized by a higher oxide of manganese, and probably in this case the presence of about 1 per cent of  $Mn_2O_3$  has served to complement the green color which would be expected from the large percentage of the acmite molecule.

## Violan.

In 1833 Breithaupt<sup>+</sup> described a mineral of rare occurrence at Piedmont, to which, from its beautiful blue color, he gave the above name. No chemical analysis was given but only a description of its physical and pyrognostic characters.

Des Cloizeaux<sup>‡</sup> has given a brief description of the crystals, on which he was able to identify in the prismatic zone the forms 100, 010, 110 and 120, as well as a prismatic cleavage,

\* Bull. Soc. Min. de France, iv, 1881, p. 157. Also Dana's System of Min., Sixth edition, analysis 26, page 370.

all corresponding closely in their angles to pyroxene. He also presents an analysis by Damour which, as the material was impure from the presence of a fibrous mineral supposed to be tremolite, he regards as only approximate. Later\* he showed that the optical properties were like those of diopside and presented an additional analysis by Pisani. A chemical analysis has also been made by Schluttig.† The analyses, all of which are given on page 357 of the sixth edition of Dana's System of Mineralogy, show considerable variation and do not yield a satisfactory formula.

In studying out the relations of the light colored pyroxene associated with alurgite, to the other members of the pyroxene family, it seemed to show a similarity to violan, especially as the analyses showed that they were both rich in soda and contained manganese and sesquioxides. As there was an excellent specimen of violan in the collection of Prof. Brush it seemed best to make a new analysis of it. The material was selected by hand and after crushing and sifting to a uniform grain it was separated by means of barium mercuric iodide solution. The portion that was taken for analysis varied in specific gravity between the limits 3.272 and 3.237. As given by other authors it varies from 3.21 to 3.233. The material when examined under the microscope was apparently very pure. The color was a beautiful light blue. The analysis is as follows:

	Ratio.	$NaR(SiO_3)_2$ .	$CaMg(SiO_3)_2$ .
SiO <sub>2</sub> 53.94	·899	·084	•815
Al <sub>2</sub> O <sub>3</sub> 1.00	$\left. \begin{array}{c} \cdot 010 \\ \cdot 005 \\ \cdot 006 \end{array} \right\} \cdot 021$		
Fe.O86	005 $021$	·021	
Mn <sub>2</sub> O <sub>3</sub> •88	•006)		
MnO ·36	$\left. \begin{array}{c} \cdot 005 \\ \cdot 416 \\ \cdot 425 \end{array} \right\} \cdot 846$		
MgO 16.63	$\cdot 416 > \cdot 846$		·846
CaO 23.80			
Na <sub>2</sub> O 1.22	$\left. \begin{array}{c} \cdot 020 \\ \cdot 001 \end{array} \right\} \cdot 021$	.021	
K <sub>0</sub> O05	·001 5 021	021	
Ign			
99.40			

These results differ from those of other investigators in showing less alkalies and sesquioxides. Moreover the identity which Igelström<sup>‡</sup> has sought to establish between violan and the mineral from Jakobsberg, Wermland, described by him<sup>§</sup>

\* Manual de Minéralogie, vol. ii, 1874, p. xix.

+ Inaug. Diss. Leipzig, 1884. Zeitschr. Kryst., vol. xiii, p. 74.

‡ Jahrb. f. Min., 1890, 2, p. 270. § Jahrb. f. Min., 1889, 2, p. 36.

under the name anthochroite is not confirmed by this analysis inasmuch as there is a marked difference in the ratio of the alkalies to the sesquioxides. As may be seen from the ratio in the author's analysis the alkalies and sesquioxides are present in the proportion 1:1, suggesting a molecule of the jadeite type, while MgO and CaO are also present as 1:1 as in normal diopside. Taking from the total ratio Na<sub>2</sub>O:  $R_2O_3$ : SiO<sub>2</sub> =  $\cdot 021: \cdot 021: \cdot 084 = 1:1:4$ , there remains MnO + MgO +CaO: SiO<sub>2</sub> =  $\cdot 846: 815 = 1\cdot 04:1$  or nearly 1:1 as required by diopside. The composition of violan may therefore be expressed as a mixture of the following metasilicates.

Diopside	$MgCa(SiO_a)_2$	90.8	per cent.
Jadeite	$NaAl(SiO_3)_2$	4.1	
Acmite	NaFe(SiO <sub>3</sub> ),	2.4	66
?	$NaMn(SiO_3)_2$	2.7	"

The mineral is therefore essentially a blue variety of diopside, containing small quantities of various well recognized pyroxene molecules.

An azure blue pyroxene has recently been described by Merrill and Packard<sup>\*</sup> from the Middle Gila, New Mexico. Their analysis corresponds essentially tc a normal diopside, with only 1.11 per cent of FeO and the blue color is regarded by them as due to the ferrous iron.

Laboratory of Mineralogy and Petrography, Sheffield Scientific School, June, 1893.

## SCIENTIFIC INTELLIGENCE.

## I. CHEMISTRY AND PHYSICS.

1. On the Absorption-spectra of Copper salts. — The absorption-spectra of aqueous solutions of copper chloride, sulphate and nitrate have been examined by EWAN, using Krüss's universal spectrometer for the purpose and employing Vierordt's method. The conclusions reached in the investigation may be summed up as follows: (1) On diluting their solutions the absorption-spectra of all the three salts examined are observed to change; (2) the character of these changes is such as to show that the spectra, in dilute solutions tend to become identical; (3) the behavior of the salts examined leads to the conclusion that in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light whilst in dilute solutions they act independently in doing so; (4) these results are substantially in agreement with the hypothesis of electrolytic dissociation; (5) and finally the results obtained do not seem to

\* This Journal, III, xliii, 1892, p. 279.

be satisfactorily explicable upon the hypothesis of a hydrolytic dissociation or on that of molecular aggregates.—*Phil. Mag.*, V, xxxiii, 317; J. Chem. Soc., lxiv, II, 149, April, 1893. G. F. B.

2. On the Separation of Gases from each other under the influence of the Electric discharge.—It has been observed by BALY, that on passing the electric discharge through a vacuumtube containing only a small quantity of hydrogen the hydrogen lines are observed only in the spectrum of the negative glow and not at all in the body of the tube. This as he shows is due to an accumulation of the hydrogen about the negative electrode; and by employing tubes of suitable shape containing mixtures of carbon dioxide and hydrogen at about 0.75mm pressure, he has succeeded in effecting so complete a separation of the hydrogen that, on sealing off the portion of the tube containing the positive electrode, only a trace of hydrogen can be detected in it by spectroscopic tests. Mixtures of hydrogen with other gases, such as nitrogen, carbon monoxide, sulphur dioxide, iodine, and mercury vapor behave similarly. When a mixture of carbon monoxide and carbon dioxide is used, the former gas separates at the negative electrode. When nitrogen is mixed with the carbon dioxide, the separation of the two is very complete. Moreover sulphur dioxide and carbon dioxide may be thus separated. Air must be highly rarefied before separation begins and then the oxygen appears to go to the negative electrode. No relation could be observed between the molecular masses of the constituent gases and the separation of the mixtures. The author points out an apparent connection between this kind of separation and striated discharges; the striæ being strongly marked only when separation occurs and never appearing if the contents of the tube remains homogeneous. If the negative electrode be made a mere point so as to prevent the formation of a glow around it, no striation nor separation is observed. Moreover pure gases do not stratify, iodine, sulphur, arsenic and mercuric iodide giving only a phosphorescence throughout the tube. Prepared in a state of considerable purity, hydrogen itself showed but traces of striation; and from this the author concludes that pure hydrogen would not stratify at all, stratification being a phenomenon due to the separation of two gases .- Phil. Mag., V, xxxv, 200; J. Chem. Soc., 1xiii, II, 253, June, 1893. G. F. B.

3. On the Determination of Molecular Mass from the Rate of Evaporation.—It is well known that when a non-volatile substance is dissolved in a fairly volatile liquid, the rate of evaporation of this liquid is decreased. This result may probably be attributed to the fact that in the case of the solution, the surface exposed is composed partly of the molecules of the volatile solvent and partly of the molecules of the non-volatile dissolved substance; while when the solvent alone is exposed to evaporation its surface consists wholly of volatile molecules. Evidently therefore the greater the number of non-volatile molecules the less the evaporation. In other words, the rate of evaporation of such a solution will decrease regularly with its concentration and will be inversely proportional to the molecular mass of the dissolved substance. Hence the molecular mass of any substance may be determined from the rate of evaporation of one of its solutions, as it may from the depression of the freezing point. KRONBERG has experimented to determine the best conditions required to put this method into operation. To make a determination, weighed quantities of two solutions, one of a substance of known, the other of a substance of unknown molecular mass, in the same solvent, should be exposed, either in the open air or in a vacuum for a given time and then reweighed. The losses in each case, calculated for one hundred parts of the pure solvent, will be inversely proportional to the molecular masses of the dissolved substances; and since one of them is known the other is readily calculated.-Monatsb. Chem., xiv, 24; J. Chem. Soc., lxiii, 261, June, 1893. G. F. B.

4. On the Boiling and the Freezing points of Nitrogen monoxide.-RAMSAY and SHIELDS have determined with care the temperature at which liquid nitrogen monoxide boils and the temperature at which it solidifies at ordinary atmospheric pressure. For this purpose they employed a hydrogen thermometer, readings of the pressure being taken at constant volume. The error arising from the difference of temperature between the stem and the bulb and that due to the alteration in the volume of the bulb were eliminated by the method used. The plan adopted was to read the position of the mercury in the capillary stem when the bulb was immersed in water at atmospheric temperature; to raise it to about 100° by covering it with cotton-wool and exposing it to the steam of boiling water and to read the increase of the pressure of the gas; and then to immerse it in the boiling nitrogen monoxide and again to read the pressure, which then of course is reduced. Three determinations of the boiling point made in this way gave the values -90.1°, -89.8° and -89.5°; the mean being -89.8°. The liquid should be kept actively boiling during the pressure reading, in order to prevent superheating. The solid nitrogen monoxide was produced by covering the bulb of the hydrogen thermometer with cotton-wool and dipping it into the liquid. On removing it and blowing air on the surface the liquid froze and the temperature fell, the pressure falling concurrently. The lowest reading of pressure was taken as equivalent to the melting point of the solid. The temperatures thus observed in two experiments were  $-102.5^{\circ}$  and  $-102.1^{\circ}$ ; the mean being  $-102.3^{\circ}$ , which may be taken as the fusing point of solid nitrogen monoxide .- J. Chem. Soc., lxiii, 833, June, 1893.G. F. B.

5. On the Tests for Arsenic.—In 1851 Fleitmann showed that when a mixture containing arsenic and antimony is added to a solution of caustic alkali and heated, arsine is evolved but no stibine. Hager soon after showed that when the arsenic is in the form of arsenic acid no arsine is evolved under these circumstances. In 1873 Gatehouse proposed to replace the zinc by aluminum in Fleitmann's test; and in 1878 Johnston claimed that this process was successful with arsenic compounds. Fresenius confirmed this result later and concedes that the Gatehouse This subject has now been reprocess detects arsenic acid. examined by CLARK who concludes from carefully conducted experiments that when arsenic acid is heated with pure aluminum and potassium or sodium hydrate not a trace of arsine is evolved; the result obtained by Fresenius being due apparently either to the presence of a little arsenous acid in his arsenate or to phosphorus. The author tested the suitability of this process for the quantitative determination of arsenic as arsenous acid. But he was unable to convert more than four-fifths of the arsenous oxide into arsine owing to the formation of the solid hydride. Moreover the author finds that the use of sodium amalgam in place of aluminum as proposed by Davy in 1876, does not evolve arsine when the arsenic present is in the form of arsenic acid.

CLARK has also proposed an improvement in Reinsch's test for arsenic. The material to be tested is boiled gently in a porcelain vessel with dilute hydrochloric acid and a strip of copper foil about 1 inch by  $\frac{1}{4}$  inch. When the coating is decided the copper is removed and washed with water and alcohol, and then placed in a mixture of dilute potassium hydrate and hydrogen peroxide and allowed to digest in the cold. The arsenic and antimony are dissolved, and the copper now bright is returned to the organic mixture. The alkaline liquid is heated to boiling, filtered and evaporated to a small bulk. It is washed into a small flask with strong hydrochloric acid, ferrous chloride is added, and the flask being fitted to a worm condenser, the arsenic is distilled into water. Through this distillate hydrogen sulphide is passed; when if more than 0.1 mgrm of arsenic be present a yellow precipitate is obtained. This may be filtered off, washed with  $CS_2$ , alcohol and water, dissolved off the filter with dilute ammonia, evaporated to dryness and weighed as arsenous sulphide. According to Curtmann, a yellow coloration is produced by hydrogen sulphide when only 0.001<sup>mgrm</sup> of arsenous sulphide is present. The filtrate after removal of the arsine is saturated with hydrogen sulphide, the antimony sulphide filtered off, dissolved in caustic soda, filtered to remove any copper sulphide, and the antimony sulphide precipitated by hydrochloric acid; the precipitate being washed with alcohol, CS, and water and weighed as antimonous In his arsenic experiments, 0.004, 0.001 and 0.0004 sulphide. gram of arsenic being taken, 0.0042, 0.0014 and 0.0004 gram were found, the latter estimated by color. In the case of antimony 0.004 and 0.001 being taken 0.0049 and 0.0017 were found. In presence of organic matter 0.004 gram each of arsenic and of antimony were taken; the quantities found being 0.0038and 0.0042 gram respectively. In a second experiment where 0.001 gram of each was taken the arsenic found was 0.001 and the antimony 0.0009. This sensitiveness appears to be all that is

required for toxical purposes.—J. Chem. Soc., lxiii, 884, 886, June, 1893. G. F. B.

6. On the Density of Carbon monoxide and the Atomic Mass of Carbon.-The density of carbon monoxide has been carefully determined by LEDUC. It was prepared by the action of sulphuric acid on oxalic acid and was purified by means of potassium hydroxide and dried over phosphoric oxide. Three mass determinations of a given volume of the gas at 0° and 760mm gave the values 2.8470, 2.8478, 2.8469; the mean being 2.8469. Since the mass of air contained in the same vessel was 2.9440 grams, the relative density of the carbon monoxide is 0.96702; agreeing with the value ordinarily accepted. If at 0°, this gas has the same molecular volume as oxygen, the atomic mass of carbon calculated from the above density is 11:913 (O = 15:88). This value agrees very closely with the numbers 11.915 and 11.917, obtained by synthesis by Van der Plaat and Friedel respectively. Assuming the experimental results to be correct, the ratio of the molecular volume of carbon monoxide to that of oxygen is 1.0001. It has been shown that the corresponding ratio for hydrogen and oxygen is about 1.002. If Regnault's value for oxygen (1.10563) be assumed as true, the atomic mass of carbon would be 11.897, which is not in sufficiently close agreement with the actual de-There can be little doubt therefore that the terminations. author's value 1.1050, is more correct. Since the relative density of methane calculated from its molecular mass is 0.55376, which is lower than the value generally accepted, it is probable that the determinations were made with a gas not quite pure. -C. R., cxv,1072; J. Chem. Soc., lxiv, 165, April, 1893. G. F. B.

7. On the Volatilization of Silica.-Although pure silica is sometimes observed in the higher portions of blast-furnaces as a sublimate, no direct experiments have ever been made apparently to test its volatility directly. This has now been done by CRAMER, who used pure crystallized native silica for this purpose. A Deville furnace, 12<sup>cm</sup> in diameter and 33<sup>cm</sup> high was heated by means of graphitic carbon, a blast of air being forced in from below. After two hours the heat obtained was equal to the highest ever noticed in furnaces, platinum not only being melted but actually beginning to boil and evaporate. A weighed quantity of the crystallized quartz was introduced into a graphitic crucible provided with a lid. This was put inside a second crucible of magnesite, the space between them being filled with powdered magnesia. The whole was now placed in the furnace, a strong blast was applied and after 4 kilograms of graphite had been burned the experiment was stopped and the quartz re-weighed. It was found to have lost 40.5 per cent. After repeating the operation three times the author succeeded in volatilizing the quartz completely. No volatilization however takes place when the temperature is not above that of melting iron.-Zeit. angew. Chem., 1892, 484; J. Chem. Soc., lxiii, 164, June, 1893. G. F. B.

8. On the Inertness of Quicklime.-While the activity of calcium oxide toward water is so well known as to give to this substance the name "quicklime," yet to other substances it is in general quite inert. Neither carbon dioxide nor hydrogen sulphide for example will unite with dry quicklime. VELEY has undertaken an investigation to determine how far the absorptive power of lime for gases is dependent (1) upon the mass of water present and (2) upon the temperature. In the first set of experiments carbon dioxide was the gas employed; in the second set sulphur dioxide. The lime was contained in a tared U tube, and the carefully dried gas passed over it. The amount of absorption was determined both by the increase of the weight of the lime and by that of a soda solution placed beyond it; the sum of the two giving the total mass of gas passed. It was observed that the effect of a trace of water is precisely similar to that of heat energy in inducing the combination of ordinarily inert substances. Neither carbon dioxide nor sulphur dioxide combines with dry lime appreciably below 350°; these gases being quite similar in this regard. At ordinary temperatures incompletely hydrated lime does not combine with  $\dot{CO}_2$ ; though 10 per cent of water greatly increases the absorption. Neither does ordinary quicklime absorb nitrous fumes.-J. Chem. Soc., lxiii, 821, June, 1893. G. F. B.

9. Lecture-notes on Theoretical Chemistry. By F. C. WRICH-MANN, Ph.D. 12mo, pp. xiv, 225. New York, 1893 (John Wiley & Sons) .- In compiling this little manual the author has evidently intended to offer within a small compass a general review of "the wide domain of chemical theory" including in this term not only chemical theories proper but also the physics of chemistry to a large extent. Hence it contains chapters on Specific gravity, on Solutions, on Energy and on Thermo-, Photo- and Electro-chemistry as well as chapters on Atoms and Valence, on Chemical formulæ, on Chemical equations and on the Periodic Law. While of course these subjects can be treated only very briefly within the space given them, they appear to be clearly presented; so that the student will be prepared for the more extended treatises, a list of which is appended. Mechanically, the book is excellent. G. F. B.

10. A Guide to Stereochemistry, based on lectures delivered at Cornell University. By ARNOLD EILOART, Ph.D., B.Sc. Svo, pp. iv, 106. With 50 woodcuts and 5 plates. New York, 1893 (Alexander Wilson). This brochure is a timely resumé of the evolution of one of the most important subjects occupying the attention of chemists at the present time. Its first 36 pages treat of the Stereochemistry of Carbon and the next 14 of the Stereochemistry of Nitrogen; while the rest of the book is occupied with an Index to the literature of Stereochemistry and a short The dearticle on the use of models in teaching solid formulas. velopment of the subject is mainly historic. The discussion is clear and, aided by the numerous illustrations, cannot fail to be fully understood by the attentive student. G. F. B.

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11. Heat. By MARK R. WRIGHT. 12mo, pp. x, 336. New York, 1893. (Longmans, Green & Co.).—This book forms one of the manuals issued for students in advanced classes. It treats the subject from the basis of fact rather than of theory, the nature of heat not being discussed until the second third of the volume. The statements appear accurate and the illustrations good. Radiation is still included as a department of heat proper. Numerous questions and problems are given at the end of the chapters. The subject of Thermodynamics is exceptionally well treated. G. F. B.

12. A Select Bibliography of Chemistry, 1492-1802, by H. C. BOLTON. 1212 pp. 8vo, No. 850 of the Smithsonian Miscellaneous collections.—This volume is the result of an immense amount of careful work. Coming from Prof. Bolton, it is sure to be accurate work. Chemists owe him a great debt of gratitude for this "labor of love."

13. Interferences of electrical waves produced by normal reflection from a metallic plate.-According to the researches of Hertz, long electrical waves apparently travel faster in air than along wires, while the velocities in the two media are sensibly equal for short waves ( $\lambda = 30^{\text{cm}}$ ). MM. Sarasin and de la Rive have instituted experiments on a large scale to test the question of this inequality in the rate of propagation. A building connected with forces motrices du Rhône at Geneva was placed at their disposal. A metallic reflecting surface 8<sup>m</sup> in height and 16<sup>m</sup> in breadth of zinc <sup>5mm</sup> in thickness was placed against a wall of the interior of the building, and a camera-like box 10<sup>m</sup> long and 1.50<sup>m</sup> wide made of black paper rested against the metallic surface and projected into the room. This dark chamber was supported at such a height that a normal through its center to the metallic surface was 4<sup>m</sup> above the floor. A species of optical bank ran through the center of the dark chamber on which the various resonators which were used were mounted.

The apparatus for producing the electric sparks did not differ essentially from that employed by Hertz with the exception that the Ruhmkorf coil was excited by a dynamo machine. The spark apparatus was placed at a height of  $4^{m}$  and  $15^{m}$  from the mirror. By moving the resonators to and fro in the dark chamber, points of interference of the direct and the reflected waves were obtained. In one case a resonator of  $0.75^{m}$  in diameter was employed. It consisted of a hollow tube of copper bent into a circle. The exterior diameter of the tube was  $1^{cm}$ , and one end of the tube was provided with a suitable micrometer in order to measure the spark gap. It was found that a reflecting surface of at least  $12^{m}$  to  $14^{m}$  in length and  $8^{m}$  in height was necessary to produce the phenomena with a resonator  $0.75^{m}$  in diameter, and a surface  $8^{m}$  by  $8^{m}$  to produce them with a resonator  $0.05^{m}$  in diameter. The author's conclusions are as follows:

The circular resonator responds to a constant wave length, whatever may be the dimensions of the exciter; the intensity of the secondary spark alone varies, attaining its maximum for a given length of the exciter. One-fourth of the wave length of a circular resonator is approximately equal to twice its diameter.

In the case of normal reflection from a metallic surface the first node is exactly at the mirror.

The velocity of propagation of an electric wave is the same for air and conducting wires.—Archives des Sciences Physiques et Naturelles, Troisiéme periode t. xxix, April and May 1893, p. 358-441. J. T.

## II. GEOLOGY AND MINERALOGY.

1. The Geological Society of America.—The fifth summer meeting of the Geological Society of America was held on Tuesday and Wednesday (Aug. 15 and 16) in the Geological Section Room of the University of Wisconsin. In the absence of the President, Sir WM. DAWSON, the Vice-President, Prof. T. C. CHAMBERLIN presided. Prof. C. R. VAN HISE gave an address of welcome.

Papers were read by J. W. DAWSON, on the study of fossil plants (read by the secretary); E. W. CLAYPOLE three short papers on fishes from the Cleveland shale; J. J. STEVENSON, on the Origin of the Pennsylvania anthracite; C. W. HALL and F. W. SARDESON, on the Magnesian series of the northwestern states; C. R. VAN HISE, on the Succession in the Marquette Iron district of Michigan; G. F. WRIGHT, on the Extra-moraine drift in New Jersey; A. A. WRIGHT, on the Limits of the glaciated area in New Jersey; J. W. SPENCER, on Terrestrial subsidence in the southeast part of the American continent; WARREN UPHAM, Evidence of elevation of Kames, Eskers, and Moraines of the North American ice sheet, chiefly from its englacial drift, and on the Succession of pleistocene formations in the Mississippi and Nelson river basins; N. H. DARTON, on the Cenozoic history of Eastern Virginia and Maryland; E. H. WILLIAMS, on South Mountain glaciation; H. F. REID, on the Gravels of Glacier Bay, Alaska; W. P. BLAKE, on the Dislocations in the strata of the Lead and Zinc Region of Wisconsin, and their relations ot the mineral deposits, with some observations upon the origin of the ores; J. H. HOLMES, on the Sand Hill country and the coastal plains of North Carolina; G. H. WILLIAMS, on the Geological exhibitions at the World's Fair; (read by title) J. P. SMITH, on the Arkansas coal measures in their relation to the Pacific Carboniferous province.

The following notes briefly indicate the contents of some of the papers read :

Prof. J. J. Stevenson, in his paper on the Origin of the Pennsylvania anthracite, described the geological structure of the coal areas of Pennsylvania and their relation to the coal areas of Maryland and the Virginias. He told of the decrease in volatile combustible matter of coals along an east and west line in Pennsylvania as described many years ago. The theory of H. D. Rogers that the anthracite is due to metamorphic influence of steam and superheated gases escaping from crevices: that of J.P. Lesley that the metamorphism is due to increased earth heat: and the other that the metamorphism is due to transformed mechanical force were examined and in each case found to be unsatisfactory, being either discordant with the facts or unsupported by them. The author maintained that the coal is not due to metamorphism but to longer continuance of the process whereby bituminous coal is formed. Twenty years ago he was led to believe that the great coal marsh, which was the parent of the successive coal beds originated at the east, and after each subsidence advanced seaward once more upon the new deltas. Under such conditions the thickness of coal in the northeast corner of the Appalachian basin, where the deltas formed rapidly, should be very much greater than in any other portion, and therefore the degree of conversion should be greater there than elsewhere. Comparisons of the several groups of the coal measures show that in the anthracite strip the thickness increases northward slowly until beyond the southerly prong of the southern anthracite field; but that the increase is abrupt at that point and soon becomes very great; also that the thickness of coal decreases westwardly as the distance increases from the anthracite region. Comparison of analysis shows that the amount of volatile matter decreases toward the anthracite region, toward the region of greatest thickness of coal; and that the decrease is gradual, even in the anthracite strip, until the thickness increases abruptly. It was shown that the decrease in volatile material has no relation whatever to increase or decrease of disturbance in the rocks: that it is wholly independent of the general composition of the associated rocks: that it is not due to the influence of heat as a metamorphic agent: but that it is due to longer exposure, prior to entombment, to conditions favoring the escape of CH.-Author's abstract.

Messrs. Hall and Sardeson classified the lower formation of Iowa, Wisconsin and Minnesota, from studies of their own in the field and of the fossils discovered, as follows:

#### Silurian.

Saint Peter (= Chazy). Shakopee (Upper Shakopee).

Upper Cambrian.

New Richmond (Elevator B Sandstone). Oneonta (Lower Shakopee) (= Low. Calcif. of N. Y.) Jordan Sandstone (= Madison sort). Saint Lawrence dolomites (= Mendota dolomites).

*Middle Cambrian.* Dresbach Sandstone.

They found a Chazy fauna in the Saint Peter; in the Shakopee a peculiar fauna which they were unable certainly to locate in the Cambrian or Lower Silurian; no fossils in the New Richmond; a common fauna in the Oneonta, Jordan and Saint Lawrence formations. The Oneonta is the basal member of the Magnesian of earlier writers.

The paper by E. H. Williams announced the discovery of a new locality of extra-morainic drift at South Mountain near Bethlehem, Pennsylvania.

A. A. Wright reported the tracing of the boundary of the moraine in New Jersey through Riggleville, Pattenburg (White House), Readington to Somerville.

Prof. G. F. Wright's paper on the Extra-Morainic Drift of New Jersey touched upon the continuity of the deposit from the moraine to the extreme border, and called attention to the need of a revised interpretation of the gravel deposits along the Delaware River. Now that the glacial border is brought down several miles below the mouth of the Lehigh River, the deposits in both rivers above that point heretofore classed with the Philadelphia brick clay and red gravel are seen to be connected with the presence of land ice and must be so interpreted. Below this point the gravel will not bear the sharp discrimination which has heretofore been given it, the Columbia and the Trenton being practically continuous.—Author's abstract.

J. W. Spencer, from a study of the topography of the bottom of the ocean and the position of the formation above the level of the sea, in the regions east and south of Florida, concluded that there are numerous deep transverse cañons off shore, and among the islands of the West Indies indicating extensive erosion at a time when the whole region was elevated, 2000 fathoms or more above its present level. His opinion was that the elevation occurred prior to the close of the Miocene, and that between the later Miocene and the present time there was a downward movement of this region.

In discussing the paper W. P. Blake referred to an unpublished fact that there are across Santo Domingo traces of coral reefs along sides of mountains indicating elevation to the amount of 2000 feet since Post-Pliocene began.

In the paper on Evidences of the derivation of the Kames, Eskers, and Moraines of the North American ice-sheet chiefly from its englacial drift, by Warren Upham, the massive kame hills which make up nearly the whole of the terminal moraine known as the backbone of Long Island eastward from Roslyn were shown to have been deposited at the mouths of superglacial or englacial streams, not by subglacial drainage; and other kames and eskers in New York, North Dakota and Manitoba were described, whose features imply their similar origin. In Minnesota and North Dakota the relationship of retreatal moraines to Lake Agassiz indicates likewise their englacial derivation. These examples are regarded by the author as types of the general manner of the transportation and deposition of the materials of kames, eskers, and moraines. The basal currents of the ice-sheet on the central and greater part of its area are thought to have carried much drift upward from the ground into the lower fourth or third part of the ice, the rate of its ascent being perhaps one or two degrees, which would give a rise of 90 or 180 feet in a mile. During the final melting and retreat of the ice-sheet, its large volume of englacial drift was deposited, partly as ground moraine or subglacial till carried down by descending currents in the outer part of the ice within distances estimated to range from 10 or 20 to 50 or 100 miles back from the ice boundary. Another large part of the englacial drift became exposed on the ice surface by its ablation and fell loosely as the ice melted away, forming the upper part of the till; but much of this superglacial drift was washed away by the glacial streams and deposited as the stratified gravel, sand, and clay, called modified drift.

In a second paper on the Succession of Pleistocene formations in the Mississippi and Nelson River Basins, the Lafayette formation and the Saskatchewan gravels were referred to fluvial deposition during an epeirogenic uplift initiating the Pleistocene period and culminating in the accumulation of the continental ice-sheet. The till and marginal moraines record the maximum extent and stages in the recession of the ice. Læss and other stratified drift deposits were mostly laid down during the glacial recession, being supplied from englacial drift, as likewise were the deltas of Lake Agassiz for their larger part. Depression of the land during the Glacial period and its reëlevation while the ice-sheet was retreating are well shown by the læss, the beaches of Lake Agassiz, and marine beds about Hudson Bay. (Author's abstract.)

N. H. Darton in his paper on Cenozoic History of Eastern Maryland and Virginia "gave a brief account of the topography and structure of the region, and of the salient feature of the Cenozoic members, and a summary of the history of a series of deposition intervals and tiltings in the general Cenozoic emergence. The principal feature of the paper was the announcement of the discovery of an erosion interval between the upper and lower Columbia terraces eastward due to tilting from the northwestward during the Columbia uplift. Off to the east and south the later Columbia lies on earlier Columbia, in places beautifully differentiated, in the normal sequence." (Author's abstract.)

H. F. Reid in his public lecture on "Glacier Bay, Alaska," said that Glacier Bay is the most accessible region in which to see large tidewater glaciers. There are eight glaciers which discharge bergs into its waters. The largest of these is Muir Glacier which drains an area of about 800 square miles. It is moving with a maximum velocity of about seven feet a day, and is continually discharging large icebergs from its end. It has extensive gravel deposits which present many interesting features. Its fluctuations have been great within recent times. One or two hundred years ago it extended, in common with the other glaciers of the bay, twenty miles below its present ending; and not long before that, the glaciers were so small, that valleys now barren

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and bleak, were occupied by large forests. (Author's abstract.) Mr. Reid afterwards read before the society a more detailed account of the gravels which are exposed in thick deposits standing as abrupt bluffs on the sides of the bays beyond the present position of the glacier front.

In the paper by Prof. Wm. P. Blake upon "Dislocation in the strata of the Lead and Zinc region of Wisconsin and their relations to the Mineral deposits, with some observations upon the origin of the ores," attention was directed to the observations of Percival in that field and their correctness as regards the faulting and also to a direct relation of the faulted areas to the mineral deposits as shown by the author's examination in the Shullsburg Reference was made to the recent paper by Prof. region. Jenney upon faults in the lead and zinc regions of Wisconsin and Missouri in further confirmation, but the author rejects the views of both Percival and Jenney in regard to the upward flow of mineral solutions through the faults, and adopts substantially the views of Prof. Whitney and of Prof. Chamberlin upon the original deposition of the sulphides from sea-water in the mass of the rocks and their subsequent concentration in the fissures and crevices by a downward flow of the solutions due to oxidation; but he directs attention however to the probable influence of the dislocations upon the localization of the deposits; first, by the possible direct outflow of freshwater, or by gases acting as precipitants; and second, by the destruction of organisms and the accumulation of their remains near the faults. He also directed attention to the petroleum shale, a thin layer, known as the "oilrock" which is generally the floor or bed-rock of the deposits of blende, and upon which this ore usually spreads out and ends. This petroleum, or the gases arising from it, appear to have had more influence in determining the reprecipitation of the sulphides than has hitherto been recognized. The fact that the lead and zinc region is coincident in area with the "driftless area" is regarded as good evidence of the source of the metallic solutions in the mass of the rocks which have decayed by oxidation and long exposure to the elements and have supplied metallic solutions, which have been reprecipitated at lower levels. In conclusion, attention was directed to the world-wide distribution of the ores of lead and zinc in the older limestones and dolomites as evidence of peculiar chemical conditions favoring the precipitation of the ores of these metals from sea-water. (Author's abstract.) The winter meeting of the Society will be held in Boston,

The winter meeting of the Society will be held in Boston, Mass., beginning December 27, 1893, at the rooms of the Boston Society of Natural History. Detailed information regarding the meeting will be sent by the Secretary in due time. H. s. w.

2. Geological Congress at Chicago.—At the World's Congress on Geology held in the Memorial Art Palace, Chicago, August 24th, 25th, and 26th, the following papers were read and discussions were held.

On Thursday, August 24th :

O. A. DERBY, of Brazil: The general geology of Brazil.

ADOLPH ERNST, of Venezuela: The general geology of Venezuela.

HENRY HICKS, of England: Pre-Cambrian rocks of Wales.

HEART M. AM, Canada: The classification of the rock formations of Canada, with special reference to the Paleozoic era.
A. C. LAWSON: The Cordilleran Mesozoic revolution.
C. W. HALL: The Pre-Paleozoic floor in the Northwestern States.

GEORGE H. WILLIAMS: Distribution of Pre-Cambrian volcanic rocks along the eastern border of the United States and Canada.

After discussion of the above papers, the special discussion for the day was upon the question, "Are there any natural geological divisions of world-wide extent ?"

On Friday, August 25:

A. R. C. SELWYN, of Canada: Huronian versus Algonkian.

ALFRED HARKER, England: On the migration of material during the metamorphism of rock masses

WARREN UPHAM: Wave-like progress of an Epeirogenic uplift.

O. A. DERBY, of Brazil: Eruptive phenomena of Brazil. W. J. McGEE: Genetic classification of Geology.

GEORGE F. KUX2: Precious stones and their geological occurrence. C. R. VAN HISE: The extent and lapse of time represented by unconformities. LESTER F. WARD: The Phylogeny of plants. O. JAEKEL, of Germany: The Phylogeny of the classes of vertebrates.

S. W. WILLISTON: Restoration of Clidastes (illustrated).

After the reading of the papers, the question for the special discussion of the day was, "What are the principles and criteria to be observed in the restoration of ancient geographic outlines?

On Saturday, August 26:

JAMES GEIKIE: Glacial succession in the British Isles and Northern Europe. HJALMAR LUNDBOHM, of Sweden: Glacial succession in Sweden.

ROBERT BELL, of Canada: The succession of the Glacial deposits of Canada.

T. C. CHAMBERLIN: Glacial succession in the United States.

WARREN UPHAM: Pleistocene climatic changes.

FRANK LEVERETT: Evidences of the diversity of the older drift in northwestern Illinois.

The special discussion for the day was upon the question, "What are the principles and criteria to be observed in the correlation of Glacial formations in opposite hemispheres?

#### H. S. W.

3. Geological Time.-Prof. C. D. Walcott, in his address before the Geological Section of the American Association on "Geological Time as indicated by the Sedimentary Rocks of North America," gave the following estimates of the length of time required for the formation of the grander divisions of sedimentary rocks.

For the Cenozoic, including Pleistocene, 2,900,000 years; the Mesozoic, 7,240,000 years; the Paleozoic, 17,500,000; the Algonkian, 17,500,000; the Archæan?

4. Annual Report, for 1892, on the Geological Survey of Texas, under E. T. DUMBLE.—The following parts of this fourth Annual Report of the Texas Geological Survey have recently been issued.

(1) A preliminary report on the Vertebrate Paleontology of the Llano Estacado by E. D. COPE. 88 pp. 8vo, with 23 plates. May, 1893. The vertebrate fossils described and figured are from the Dockum Terrane of the Triassic, the Loup Fork beds, the Blanco beds, and the Equus beds. They represent nearly fifty species.

(2) Preliminary Reports on the Artesian Wells of the Gulf coastal slope, by I. A. SINGLEY; and on the organic remains from the deep well at Galveston, by GILBERT D. HARRIS. 34 pp. June, 1893. The Galveston well is that which is the subject of the paper at page 38 of this volume.

(3) A contribution to the Invertebrate Paleontology of the Texas Cretaceous, by F. W. CRAGIN. 106 pp., with 13 plates.

(4) Report on Grimes, Brazos, and Robertson Counties, by W. KENNEDY. 84 pp., with sections. June, 1893.

(5) Report on the Rocks of Trans-Pecos Texas, by A. OSANN; and on the Geology of Trans-Pecos Texas, by W. H. STREERU-WIRTZ. 54 pp. July, 1893.

5. Geological Survey of New Jersey. Gasteropoda and Cephalopoda of the Raritan Clays and Greensand Marls of New Jersey, by R. P. WHITFIELD. 402 pp. 4to, with 50 plates. Trenton, N. J., 1892.—The first part of Mr. Whitfield's very valuable Report on the Cretaceous and Tertiary fossils of New Jersey, treating of the Lamellibranchiata, is now followed by a second part, of like importance and excellence. These volumes are ix and xviii in the quarto publications of the U. S. Geological Survey.

6. Annual Report of the Director of the U. S. Geological Survey, vol. XI. Part 1, Geology, 750 pp. roy. 8vo; Part 2, Irrigation, 396 pp.; each with maps and other illustrations.—The memoirs included in Part 1, are the following: "The Pliocene History of northwestern Iowa, by W. J. McGEE, occupying 380 pages—which has already been noticed in this Journal; and the Natural Gas field of Indiana by A. J. PHINNEY, 126 pp., with an introduction of 28 pp. by W. J. McGEE.

7. The following Bulletins and quarto Memoirs of the United States Geological Survey have been recently issued :---

Bulletin No. 85. Correlation Papers: The Newark System, by I. C. RUSSELL. 344 pp., 8vo, with maps.

No. 86. Correlation Papers: Archean and Algonkian, by C. R. VAN HISE. 549 pp., with maps.

No. 90. Report of work done in the division of Chemistry and Physics, mainly during the fiscal year, 1890-91, by F. W. CLARKE. 75 pp.

No. 91. Record of North American Geology for 1890, by N. H. DARTON. 88 pp.

No. 92. The compressibility of Liquids, by CARL BARUS. 96 pp., with plates.

No. 93. Some Insects from Florissant, Colorado, and from other points in the Tertiaries of Colorado and Utah, by S. H. SCUDDER. 35 pp., with plates. No. 94. The mechanism of solid Viscosity, by CARL BARUS. 138 pp., with figures.

No. 95. Earthquakes in California in 1890 and 1891, by E. S. Holden. 29 pp.

No. 96. The Volume Thermodynamics of Liquids, by CARL BARUS. 100 pp., with plates.

Memoir Vol. XVII. The Flora of the Dakota Group, a posthumous work by Leo Lesquereux, edited by H. H. Knowlton. 400 pp. 4to, with 66 plates.

8. The Seismological Journal of Japan: edited by JOHN MILNE, F.S.S. Vol. I, 1893.—This Journal succeeds to the publications of the Seismological Society, this society having ceased to exist. This volume corresponds to vol. xvii of its Transactions. As Japan is extraordinary as regards frequency of earthquakes, and also their violence, its Seismological Observatory and 700 outside stations are capable of more thorough investigation in this department than is elsewhere possible. The work already done has produced, for future investigators, new seismographs giving absolute measurements of earth-motions, and has led to the application of principles for the mitigation of the effects of earthquakes on buildings, besides advancing seismological science in other ways. This volume of 150 pages contains various papers of value by Mr. Milne, and others by Prof. W. K. Burton, and F. Omori.

9. Bulletin of the Geological Institution of the University of Upsala, edited by HJ. SJÖGREN. No. 1, Vol. I, Upsala, 1893. 95 pp. with 5 plates.—This new publication, of which the first number has recently appeared, is designed as a medium for the issue of original investigations made at the University of Upsala. The leading and longest article (pp. 1–64) is entitled Contributions to Swedish Mineralogy by Hj. Sjögren and contains the results of his observations upon the species of the humite group from Sweden, also on svabite, adelite, etc. Other articles, chiefly geological, are by Wiman, O. Nordenskiöld, Anderson, etc.

10. Traité des Gîtes Minéraux et Métallifères ; recherche, étude et conditions d'exploitation des mineraux utiles, description des principales mines connues, usages et statistique des Métaux. Cours de Géologie Appliquée de l'École supérieure des Mines; par ED. FUCHS, Ingénieur en chef des Mines, Professeur à l'Ecole supérieure des Mines, et L. DELAUNAY, Ingenieur au Corps des Mines, Professeur à l'Ecole supérieure des Mines. Paris, 1893 (Baudry et C<sup>ie</sup>). Large 8vo, vol. i, 823, pp., vol. ii, 1015 pp. with many maps and illustrations.—This treatise of over 1800 octavo pages, on useful minerals and ores, their distribution, modes of occurrence, methods of origin, and the industrial subjects connected with them and their exploration, is an admirable work. After an introduction of 110 pages, consisting of an alphabetic list of localities, a table giving the geographical distribution of localities over the globe, and tables for the conversion of French and foreign weights and measures and coins, the treatise commences with Carbon, under which, the subject of the Diamond covers near 50 pages; and then follow, with full details, the subjects of natural gas, petroleum, bitumen and other hydrocarbons, carrying the work to the 220th page. Like fulness as to details characterizes the whole work. Besides descriptions, the work contains a large number of maps of the mineral regions, several of them giving the geological formations; and among these there is a colored geological map of the United States (from Hitchcock's), a map of the petroleum region of western Pennsylvania, one of the Comstock and another of the Eureka region in Nevada, another of the Leadville region, each of these, large and fine detailed maps, with sections and plans of workings. In like manner the various localities of mines and useful minerals of other countries are illustrated. The work was prepared for the course of applied geology at the École des Mines, at Paris, instituted in 1879 by Prof. Fuchs; and it is well adapted for use in such courses elsewhere.

11. The Glacialists' Magazine: A Monthly Magazine of Glacial Geology, embodying the Proceedings of the Glacialists' Association. Edited by PERCY F. KENDALL, F.G.S. and Secretary of the British Association Committee on Erratic blocks; assisted by WARREN UPHAM, C. E. DERANCE, President of the Glacialists' Association, and J. LOMAS, A.R.C.S.—This first number of the Glacialists' Magazine, covering 30 pages, contains, besides various notes on Glacial subjects, the Presidential Address of the Glacialists' Association, C. E. DeRance, and a discriminating review of Howorth's "Glacial nightmare and the Flood." The magazine, as its editorial corps indicates, will be a valuable Journal for the American as well as European side of the Atlantic.

12. Mount Loa, Hawaii.—An ascent of Mt. Loa was made by Rev. E. P. Baker on the 24th of June last. At the summit, the only action to be seen in the summit crater was the escape of vapor, great volumes of which arose from the central area, the same from which it issued from 1885 to the time of the eruption in 1887. At the time of his visit to the crater in February 1887, and again in 1888, there was a small crater in the floor of the great central crater near its southwest corner. This small crater was in existence in 1889, when the crater was visited by Mr. Thurston. But nothing was now to be seen of it; lavas had filled it, making the floor continuous over the place. Its outline only was partially distinct at two or three points in its circumference. -Letter from Mr. Baker, dated Hilo, July 5, 1893. According to an earlier letter from Mr. Baker, on November 30 and December 1 and 2 of 1892, a light was seen at the top of the mountain from below, indicating the presence in the bottom of the crater, as his letter states, of molten lava; and this may have been the time of the occurrence mentioned above.

13. Brief notices of some recently described Minerals.—NEPTU-NITE and EPIDIDYMITE are two new species described by G. Flink from the neighborhood of Julianehaab on the Kangerdluarsuk in Greenland. They occur with ægirite, arfvedsonite, eudialyte, etc., the association being similar to that of Langesund in Norway.

Neptunite occurs in short prismatic crystals, belonging to the monoclinic system, and shows perfect cleavage parallel to the fundamental prism of 99° 46'. The hardness is between 5 and 6 and the specific gravity 3.234. The color is black, but deep redbrown in very slender crystals. An analysis gave :

For this the formula proposed is :

 $(\frac{3}{4}Na_{2} + K_{3})Si_{4}O_{3} + (\frac{2}{3}Fe + \frac{1}{3}Mn)TiO_{3}$ .

*Epididymite*, as is suggested in the name, is near the eudidymite of Brögger and is regarded as a dimorphous form of the same compound. It is found in orthorhombic crystals prismatic in the direction of the macrodiagonal, and pseudohexagonal in angle, which character is also shown in its twinning. The angles and axial ratio are not far from those of eudidymite, which, however, has been referred to the monoclinic system. The composition is the same, namely:  $HNaBeSi_sO_s$ . An analysis gave :

	$SiO_2$	BeO	$Na_2O$	$H_2O$
Sp. Grav.=2.548	73.74	10.56	12.88	$3.73 \pm 100.91$

-Geol. För. Förh., xv, 195, 1893.

14. HAUTEFEUILLITE is a hydrated phosphate of magnesia and lime from the apatite mines of Bamle, Norway, described by L. Michel. It occurs in lamellar masses having a radiated structure and made up of minute monoclinic crystals elongated vertically and flattened parallel to the clinopinacoid. The hardness is 2.5, the sp. gravity 2.435 and it is colorless and transparent. The analysis gave:

 $\begin{array}{ccccccc} P_2O_5 & MgO & CaO & H_2O \\ 34{\cdot}52 & 25{\cdot}12 & 5{\cdot}71 & 34{\cdot}27{=}99{\cdot}62 \end{array}$ 

This corresponds to the formula  $(Mg,Ca)_{*}P_{*}O_{*}+8H_{*}O$ , which brings it near bobierrite. The name is given in honor of M. Hautefeuille.—*Bull. Soc. Minn.*, xvi, 38, 1893.

15. MELANOSTIBIAN is an imperfectly investigated mineral from the manganese mine, Sjögrufvan, in Örebro, Sweden; it is described by L. J. Igelström. It occurs in massive form either with foliated structure forming thin veins, or in microscopic crystals for which the tetragonal or orthorhombic system is suggested. The hardness is 4, the color black, and it is opaque with metallic luster. An analysis (assuming the iron and manganese present as protoxides and the antimony as Sb<sub>2</sub>O<sub>3</sub>) gave:

Sb <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	$H_{2}O$
37.50	27:30	29.62	1•97	1.03	1.06=98.48
-Zeitschr.	f. Kryst.,	xxi, 246,	1893.		

16. Snow Crystals.—A recent paper by G. Nordenskiöld gives the preliminary results of an investigation in the winter of 1892-93 of the forms of snow crystals. The discussion of general conclusions is deferred for a later article, but the results as given show a much higher degree of complex character than has ordinarily been assumed. The crystals are divided into two groups according as the development is in the direction of the vertical axis or tabular, and several varieties are noted under each. The paper is illustrated by 20 excellent photo-plates showing many types of forms; most of the crystals are magnified several diameters.— Geol. För. Förh., xv, 146, 1893, and Bull. Soc. Min., xvi, 59.

17. Repertorium der mineralogischen und krystallographischen Literatur von Anfang d. J. 1885, bis Anfang d. J. 1891; und Generalregister der Zeitschrift für Krystallographie und Mineralogie, Band xi-xx. Herausgegeben und bearbeitet von P. GROTH und F. GRÜNLING. II Theil. 287 pp. 8vo. Leipzig, 1893 (W. Engelmann).—The second part of this important work (see this Journal, May, 1893, p. 442) has recently been issued. It contains the topical index by Dr. Grünling to volumes xi to xx of Groth's Zeitschrift für Krystallographie und Mineralogie.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. American Association for the Advancement of Science.— The forty-second meeting of the American Association was held at Madison, Wisconsin, from the 16th to the 22d of August; about three hundred members registered. The President of the meeting was Prof. William Harkness of Washington. The Vice-Presidents, with the subjects of the addresses delivered by them before their respective sections, are as follows :

- A, MATHEMATICS AND ASTRONOMY-C. L. Doolittle, of South Bethlehem, Pa., on Variations of Latitude.
- B, PHYSICS-E. L. Nichols, of Ithaca, N. Y., on Phenomena of the Time Infinitesimal.
- C, CHEMISTRY-Edward Hart, of Easton, Pa., on Twenty-five Years' Progress in Analytical Chemistry.
- D, MECHANICAL SCIENCE AND ENGINEERING-S. W. Robinson, of Columbus, Ohio, on Recent Advances in Mechanical Science.
- E, GEOLOGY AND GEOGRAPHY—Chas. D. Walcott, of Washington, D. C., on Geologic Time as Indicated by the Sedimentary Rocks of North America.
- F, ZOOLOGY—Henry F. Osborn, of New York, N. Y., on The Rise of the Mammalia.
- G, BOTANY-Charles E. Bessey, of Lincoln, Neb., on Evolution and Classification.
- H, ANTHROPOLOGY-J. Owen Dorsey, of Tacoma Park, Md., on the Biloxi Indians of Louisiana.

I, ECONOMIC SCIENCE AND STATISTICS—William H. Brewer, of New Haven, Conn., on The Mutual Relations of Science and Stock Breeding.

The address of the retiring President, Professor Joseph LeConte of Berkeley, California, upon the Origin of Mountains, was delivered Thursday evening, August 17th.

Saturday was devoted to excursions to several points in the vicinity of Madison, no long excursions being undertaken because of the Scientific Congresses at Chicago, which followed the Association.

Upon the recommendation of the Geological Section, a standing committee on recording and classifying fossil faunas and floras was appointed by the Association, consisting of Henry S. Williams (chairman), Henry F. Osborn (secretary), Chas. D. Walcott, Saml. H. Scudder and Arthur Hollick, with power to add to their number.

The Association elected, as its president for the next meeting, the anthropologist, Dr. D. G. BRINTON, of Media, Pa.; and as officers of Section E, Prof. SAMUEL CALVIN, of Iowa City, Iowa, vice-president, and Prof. W. M. DAVIS, of Cambridge, Mass., Secretary. The meeting will be held in August, 1894; and it is understood that its place, though not decided upon, will be some city in the Eastern States.

## List of papers accepted for reading.

#### Section A. Mathematics and Astronomy.

FRANK H. LOUD: A construction for the imaginary points and branches of algebraic loci.

ALEX. S. CHRISTIE: Upon the latitude variation tide.

E. W. HYDE: The screw as a unit in a Grassmannian system of the sixth order.

ALEX. MACFARLANE: Applications of the generalized logarithmic theorem.

L. E. DICKSON: On the inscriptions on regular polygons.

C. L. DOOLITTLE: Latitude determination at Bethlehem, 1892-93.

GEO. C. COMSTOCK: A determination of the constant of aberration by a modified form of the Loewy method.

MANSFIELD MERRIMAN: On the possibility of the algebraic solution of the general equation of the fifth degree.

S. S. LAWS: Space.

#### Section B. Physics.

E. W. MORLEY and WM. A ROGERS: Application of interferential methods to measurements of expansion of long bars.

W. A. ROGERS: A preliminary study of the constants of the Morley interferential comparator. On the effect of evaporation upon the relative dimensions of bars of metal partially submerged in water.

ALEXANDER MACFARLANE: On physical addition or composition.

G. S. MOLER: Some rapid changes of potential studied by means of a curvewriting voltmeter.

E. L. NICHOLS: Some applications of electric heating in physical laboratory practice. Note on the surface tension of liquids.

E. L. NICHOLS and G. S. MOLER: An apparatus for the generation of oxygen and hydrogen by electrolysis.

ERVIN S. FERRY: Note on the use of a rotating disk in photometry.

F. BEDELL, K. B. MILLER and W. F. WAGNER: Irregularities in alternate current curves.

FREDERICK BEDELL: Experiments with an alternate current condenser.

J. O THOMPSON: On the elasticity of metals. Fatigue in the elasticity of stretching.

A. MACFARLANE and G. W. PIERCE: The elastic strength of solid, liquid and gaseous dielectrics.

W. S. FRANKLIN and L. B. SPINNEY: Elastic properties of glass. W. LECONTE STEVENS: On so-called negative lightning.

E. W. MORLEY: An automatic Toepler pump.

JOHN S. SHEARER: The effect of temperature and of electric driving on the period of tuning forks.

B. W. SNOW: On the continuous spectrum of the alkalies.

JOHN DANIEL: Electrolytic polarization.

#### Section C. Chemistry.

E. W. MORLEY: On the atomic weight of oxygen. W. E. STONE: The acetyl and benzoyl derivatives of the pentoses.

W. E. STONE and H. N. MCCOY: The electrolytic oxidation of glycerol. W. R. ORNDORFF and JOHN WHITE: The constitution of paraldehyde and metaldehyde.

W. A. NOYES: On the nitrites of some amines. Natural gas from New Lisbon, Ohio.

P. C. FREER: The action of sodium on acalone.

P. W. SHIMER and S. K. RIEFSNYDER: Some experiments on sampling by quartation.

L. KAHLENBURG and H. W. HILLYER: Solubility of lead oxide in the normal tartrates and other organic salts with observations on the rotary power of the solutions thus obtained.

T. B. STILLMAN: The analysis of lubricating oils containing "blown" rape-seed and "blown" cotton-seed oils.

G. B. FRANKFORTER: Narceine, a new formula and new derivatives. The structural formula for narceine and its synthesis form narcotine pseudo-norceine. E. GOLDSMITH: A tempered steel meteorite.

W. L. DUDLEY: The action of gaseous hydrochloric acid and oxygen on the platinum metals. The electro-deposition of iridium: a method of maintaining the

uniform composition of an electroplating bath without the use of an anode. E. G. SMITH: On the occurrence and distribution of nitrogen in deep artesian wells of the Mississippi Basin.

E. H. S. BAILEY and E. C. FRANKLIN: The advantages of extended examinations of river waters.

G. HINRICHS: On the systematic errors affecting all the atomic weights of stars. On a review of atomechanics.

L. ANDREWS: An unusual form of calcium glycerate.

#### Section D. Mechanical Science and Engineering.

S. W. ROBINSON: Improved form of transmission dynamometer.

J. BURKITT WEBB: Economical compression in a steam engine.

D. S. JACOBS: Experimental determination of the quickness of action of a shaft governor. Tests of automatic fire sprinklers. An accurate method of measuring heavy liquid pressure.

C. WELLMAN PARKS: A mechanical index.

HUPFEL, GRISWOLD and KENNEDY: Test of plant of the Hygeia Ice Company of New York City.

WM. A. ROGERS: On the changes in the dimensions of metals which may be due to changes in molecular structure depending on their age.

#### Section E. Geology and Geography.

H. F. REID: Gravels of Glacier Bay, Alaska, with lantern illustrations. JOHN J. STEVENSON: Use of the name "Catskill."

J. A. HOLMES: Section across the coastal plain region in southern North Carolina.

WILLIAM HALLOCK: Notes on further observations of temperature in the deep Well at Wheeling, W. Va. ARTHUR HOLLICK: Recent investigations in the Cretaceous formation on Long

Island, N. Y. Northward extension of the yellow gravel in New Jersey, Staten Island, Long Island and eastward.

E. R. VAN HISE: Character of folds in the Marquette iron district. E. W. CLAYPOLE: The fossil sharks of Ohio.

HORATIO P. PARMELEE: Hillsdale county geology.

CHAS. D. WALCOTT: Exhibition of tribolites showing antennæ and legs. JOSEPH F. JAMES: Remarks on genus Arthrophycus Hall. On the value of pseudo-algæ as geological guides. Studies in problematic organisms. The genus Fucoides.

T. C. CHAMBERLIN: Some questions respecting glacial phenomena about Madison.

D. F. LINCOLN: Amount of glacial erosion in the Finger Lake region of New York.

F. P. GULLIVER: Ice-sheet on Newtonville Sandplain.

G. FREDERICK WRIGHT: Additional facts bearing on the question of the unity of the Glacial Period.

FRANK LEVERETT: Changes of drainage in Rock River basin in Illinois.

W. J. MCGEE: Graphic comparison of post-Columbia and post-Lafayette erosion.

R. D. SALISBURY: An illustration of the effect of stagnant ice in Sussex Co., N. J. A phase of superficial drift.

WARREN UPHAM: Tertiary and Quaternary stream erosion of North America. T. C. HOPKINS: The emergence of springs.

#### Section F. Zoology.

C. V. RILEY: Notes on Aspidiotus perniciosus. Erastria scitula, a valuable insect to introduce into America. Sphida a myth.

J. B. SMITH: Seat of life in the house fly.

S. H. GAGE: The respiratory mechanism in the lamprey.

L. O. HOWARD: The correlation of structure and host-habit in the Encyrtinæ. H. F. OSBORN: The mammals of upper Cretaceous.

THEOBALD SMITH: The production of races and varieties of bacteria in mixed cultures. A new sporozon in the intestinal villi of cattle. H. G. HUBBARD: The insect guests of the Florida land tortoise. W. S. MILLER: A comparative study of the lung, with special reference to

the communication of one air-sac with another.

J. H. PILLSBURY: Some new revelations regarding color sense in the human retina. On a new apparatus for measuring the strength of color sense.

#### Section G. Botany.

G. F. ATKINSON: Photography as an instrument for recording the microscopic characters of micro-organisms in artificial cultures. Symbiosis in the roots of Ophioglosseæ. Comparative study of the structure and junction of the sporangia of ferns in the dispersion of spores.

B. T. GALLOWAY: Observations on a rust affecting the leaves of the Jersey or Scrub Pine. Results of some recent work on rust of wheat.

W. J. BEAL: Prophylla of Gramineæ.

J. CHRISTIAN BAY: A new injection needle for the study of lower plants. The bibliography of American botanical literature.

C. R. BARNES: On the food of green plants.

BYRON D. HALSTED: The Solandi printing applied to botanical work. The shrinkage of leaves in drying.

N. L. BRITTON: Present aspects of the nomenclature question. A consideration of a species based upon a theory of evolution.

T. A. WILLIAMS: Lichens of the Black Hills.

D. H. CAMPBELL: Notes on the development of Marattia Douglasii.

JOHN G. JACK: The fructification of Juniperus. M. B. THOMAS: The roots of orchids.

THEOBALD SMITH: Further observations on the fermentation tube with special reference to anærobiosis, reduction, and gas production.

ERWIN F. SMITH: Two new and destructive diseases of Cucurbita.

CONWAY MCMILLAN: Preliminary statement concerning botanical laboratories and instruction in American universities and colleges.

J. H. PILLSBURY: On the quantitative analysis of the colors of flowers and foliage.

S. G. WRIGHT: The minute structure and development of the motile organ in the leaf of the red-bud.

S. M. TRACY: Distribution of the Gramineæ in the United States. ELIZABETH G. BRITTON: A revision of genus *Physcomitrium*. On Ulota Americana Mitten and Orthotrichum Americanum Beauv.

J. C. ARTHUR: Deviation in development due to the use of unripe seeds. W. T. SWINGLE: The principal diseases of citrous fruits now being studied at Eustis, Fla. Cephaluros mycoidea and Phyllosiphon sp., two parasitic algæ new to North America.

V. COVILLE: An analysis of the conditions affecting the distribution of plants. P. H. ROLFS: A Sclerotium disease of plants.

L. H. PAMMEL: Notes on Ræstelia pyrata Crossing of Cucurbita. A case of poisoning by the wild parsnip, Cicuta maculata. Preliminary notes on some chromogenic bacteria of the Ames flora.

#### Section H. Anthropology.

WASHINGTON MATTHEWS: Songs of sequence of the Navajos. [Illustrated by the phonograph.]

H. C. MERCER: The result of excavations at the ancient argillite quarries, recently discovered near the Delaware river on Gaddes Run. Another ancient source of jasper blade material east of the Middle Alleghenies.

C. STAINLAND WAKE: Indian migrations.

W. H. BREWER: The instinctive interest of children in bear and wolf stories. E. H. S. BAILEY: The delicacy of the sense of taste among Indians.

H. I. SMITH: Caches of the Saginaw Valley. J. N. B. HEWITT: Is the polysynthesis of Duponcean characteristic of American Indian languages.

A. F. CHAMBERLAIN: Primitive woman as a poet. Some drawings by Kootenay Indians.

J. JASTROW: Psychology at the World's Fair.

H. N. RUST: Some account of a purification ceremony and a sacred stone in use among the mission Indians of California. The Indian stone Adzes. Some facts concerning the obsidian blades called swords, from northern California.

ERNEST VOLK: Observations in regard to the use of argillite by prehistoric people, made by explorations of ancient village sites in the Delaware Valley.

G. F. WRIGHT: The evidence of glacial man in America.
 W. J. MCGEE: The antiquity of man in America.

A. S. HERRERA: The prehistoric man of Mexico.

J. F. SNYDER: Buried deposits of hornstone discs.

W. E. MYER: A Shawnee town and its exploration.

W. K. MOOREHEAD: Remarks upon sheet copper designs from the Hopewell group, Ohio.

G. A. DORSEY: The ancient necropolis of Ancon, Peru. Notes for an archæological study of La Plata Island, Ecuador. A ceremony of the Quichua Indians of Peru.

D. G. BRINTON: Remarks on the Mexican Calendar System.

W. H. HOLMES: Theory of primal shaping arts.

J. O. DORSEY: Indian names for the Four Winds and Four Quarters.

C. A. HIRSCHFELDER: The sacrifice of the white dog.

M. M. SNELL: The relation between Mythopeia and Euhemerism.

ADA M. KING: Revision of calendar.

#### Section I. Economic Science and Statistics.

MANLY MILES: Surface tension of water and evaporation with experiments. Energy as a factor in nutrition.

LAURA O. TALBOTT: The utility of practical psychology. Geneo-pathological chart.

W. J. BEAL: Manual labor at agricultural colleges.

RICHARD COLBURN: The maturing Pacific railroad debts. HENRY FARQUHAR: Relations of production and price of silver and gold. H. F. J. PORTER: The necessity for a bureau of record and reference.

2. The Physical Geography of Antarctica.-The following paragraphs are from a notice of Dr. Karl Fricker's paper on "Die Entstehung und Verbreitung des antarktischen Treibeises," in the London Geographical Journal for September.

The sources of polar ice are in the main three—snow or glacier ice, fresh-water ice, and sea-water ice, with the possible addition of a fourth, the coast ice or ice foot; and, inasmuch as the relative importance of these is determined both directly and indirectly through the influence on climate, by the geographical distribution of land and sea, the south polar regions present, so far at least as is known, an almost complete contrast to the north. The northern hemisphere has a polar sea, enclosed by a polar continent except for at the most four or five openings, of which only two-Davis Strait and the channel between Iceland and Norway-are of real moment in the movement or distribution of ice, while the southern hemisphere has a polar continent surrounded by a polar ocean, to which a number of islands contribute a quite negligible fraction of the total ice. The supposed Antarctic continent has been touched by explorers in three dis-tinct regions—Enderby Land and Kemp Land in 40° to 60° E. longitude, Wilkes Land and Victoria Land 100° to 170° E. longitude, and Graham Land and Alexander I. Land, with a number of detached islands (for which Dr. Fricker proposes the name Gerritsz Archipelago) to the south of Cape Horn-and in each case it has been found to present an almost unbroken sheet of ice, varying in thickness and formation with the configuration of the land, which extends outwards from the coast and terminates in precipitious ice-cliffs, the great ice barrier.

The conditions giving rise to the formation of an ice-cap of such dimensions are chiefly, of course, those of climate, and of these our knowledge is as yet wofully meagre. Theory, as at present developed, requires a polar area of low barometric pressure—a uniform gradient downward from all sides—and a belt of westerly winds with a central calm area; and for comment we have only a few sets of observations taken during the summer months, none of which extend over more than a few weeks in one place. But so far as they go, the observations almost directly traverse the theoretical hypotheses. They indicate in the first place a zone of low pressure in about 75° S. latitude, with higher barometer further south. Hann suggests that this trough is due to the passage of moving cyclones; but the supposition is not borne out by the wind observations, which show an overwhelming majority in favor of points between S. and N.E. Since the air temperature over the continent cannot, even in summer, much exceed the freezing-point on account of the ice covering, it seems not unreasonable to suppose as an alternative that pressure continues to increase with latitude after the 75th parallel, and that the southerly and easterly winds are the overflowing currents from a permanent polar anti-cyclone. It was to be expected d priori that a theory founded on the assumption of a homogeneous land or sea surface would require modification in the circumstances, and the vertical height of the supposed anti-cyclone need not be sufficient to interfere with upper currents; it might in fact rest as a cushion on the land surface almost independent of the general circulation.

Granting the existence of the polar anti-cyclone, it is not difficult to imagine that the moist warm air ascending from the lowpressure zone moves southward and feeds the anti-cyclone, discharging large quantities of moisture as snow and sleet, and also in the form of crystals deposited from mist, as the temperature is reduced by the ice sheet; and since the supply of vapor is greatest during the more open season in the low-pressure belt, it seems likely that precipitation is greatest during summer. Such climatic conditions are fully sufficient to account for the presence of glacier ice in almost unlimited quantity, provided we assume the existence of continental land, an assumption strongly supported by our knowledge of the Arctic regions, the negative evidence of Grant's Land and the positive of Franz Joseph Land being specially pertinent.

Glaciers of the valley of Alpine type are found on the most stupendous scale. Ross describes one on the east coast of Victoria Land as filling a valley bordered by mountains 6000 to 10,000 feet in height, and sending a tongue far into the sea. But the distinctive feature is the inland ice, known as yet only by the insurmountable cliffs facing the sea. This barrier is remarkable for the uniformity of height it retains for long distances. From the volcances Erebus and Terror, Ross traced it eastward for 250 miles, and gives the narrow limits of 150 to 200 feet, Wilkes gives for other parts 150 feet, d'Urville 100 to 150 feet, and Biscoe 100 to 120 feet; in Grahamsland, on the other hand, only 12 to 14 feet is stated. Again, the barrier-ice is noted by the absence of detritus, or moraine material of any kind.

The stormy weather of the southern ocean, and the strength of the tidal streams are in themselves almost sufficient to prove that the barrier-ice is not field-ice formed at sea, but essentially inland ice, and of this further evidence may be derived from its structure. Wilkes, Webster, d'Urville, and in particular the *Challenger* Expedition, give information derived from the examination of icebergs, and agree in describing the ice as of a stratiform structure, their blue layers of hard ice alternating with thicker beds of white soft ice enclosing air, the latter thicker and softer near the top of the ice, and the former preponderating in the lower strata. Similar formations have been observed by Nansen and Payer, and the presumption is that the soft strata represent snow fallen during winter, and the hard a surface partially melted during the warmer months and re-frozen. Under great pressure the whole mass is gradually converted into homogeneous hard blue ice.

Concerning the several motions of the inland ice, we are without information of any kind. Of the various computations as to its mean thickness, Dr. Fricker adopts that of Thomson—1400 feet.

According to Heim, there are four possible agencies tending toward the dissolution of glacier ice-melting from above, melting from below, internal melting, and the breaking away of drift ice. From the considerations stated above it appears that Antarctic glaciers are chiefly exposed to the second and last of these, the action of warm water eating away the under surface, and the separation of enormous icebergs. Under the most moderate estimates, Dr. Fricker calculates that a minimum of 258,000,000,000 cubic metres of ice are annually detached from the ice barrier and set adrift. The subsequent wanderings of these bergs are chiefly controlled by the ocean currents, although the direct influence of wind is considerable; and the normal "northern limit of drift-ice" is of special interest from the amount of information relating to currents which can-due caution being exercised -be obtained from it. Taken generally, the set of the currents corresponds in direction to the prevailing winds, from south toward north, northwest and west. To this rule there are, however, important exceptions. A comparatively strong easterly current prevails to the south of Cape Horn, probably because of the strong development of west wind drift to high latitudes in the South Pacific, and the contraction of Bransfield Strait. Again, the motion of the streams becomes extremely involved in the two cases where the coast trends north and south, east of Gerritsz Land and Victoria Land, in part probably simple tidal, and in part "compensation currents" flowing southward. Neumayer to the contrary notwithstanding, Dr. Fricker admits the existence of only one true southerly current-to the south of Kerguelen-and of this he proposes an extremely ingenious explanation. Kerguelen and Head Island are connected by a range of submarine mountains some 240 miles in length, which rises to within 100 fathoms of the surface. Assuming that the westerly drift current extends below this depth, on meeting the obstacle it will divide and a part will be deflected in a south-southeasterly direction, and will to some extent retain that direction by virtue of its superiority in speed over the currents of higher latitudes. The other section of the current, deflected northward, may account for the bend of isothermal lines in that direction observed in the vicinity of Kerguelen.

The general northward tendency of the surface currents, taken along with the known presence of Antarctic water in the lower depths of the oceans of the southern hemisphere, raises a question of considerable difficulty as to the nature of the return or compensation current. Dr. Fricker offers a solution of the problem, based on the temperature observations of the *Challenger* and the Gazelle, which concur in showing a stratum of relatively warm water at depths between 700 and 900 fathoms in all oceans. The bottom water, moving slowly northward, is ultimately stopped and forced to ascend (the phenomena are naturally most fully developed in the Indian Ocean), its temperature greatly raised, and finally its density so increased by evaporation that it sinks to a position of equilibrium at an intermediate depth and flows southward, tending at the same time eastward through the Earth's rotation as a warm current. On regaining the Antarctic regions the water of this intermediate current is in part absorbed in the formation of ice, and the remainder being thereby increased in density sinks to the bottom and begins its slow return northward.

3. Prodromus Faunæ Mediterraneæ, of JULIUS VICTOR CARUS of Leipzig, vol. ii, Part III, Stuttgart, 1893 (E. Schweitzenbart'shce Verlagshandlung).—This new part of volume ii, treats of the Vertebrata, and concludes this very important Prodromus on the Fauna of the Mediterranean. Something of the value of the work may be gathered from the fact that the index of species occupies more than 100 pages, and is independent of an Index of common names covering 30 pages.

4. Bulletin of the Geographical Club of Philadelphia. Vol. 1, No. 1, pp. 1-35. January, 1893, Philadelphia.—The first number of the new publication by the Geographical Club of Philadelphia contains an interesting and well illustrated paper upon Mountain Exploration by Edwin Switt Balch.

5. The Mammals of Minnesota, by C. L. HERRICK. Bulletin No. 7 of the Geological and Natural History Survey of Minnesota, N. H. WINCHELL, State Geologist. 300 pp. 8vo.—This work is a scientific and popular account of the features and habits of the Mammals of the State, illustrated by several plates and a number of woodcuts. The first of the plates is a fine colored figure of the *Geomys bursarius*, or Pocket Gopher. A second part of the work remains to be published devoted to the materials collected on the anatomy, especially the myology and osteology, of the State mammals.

6. Ueber die Entwickelung der Theerfarben-Industrie von Dr. HEINRICH CARO. 151 pp. Berlin, 1893 (R. Friedländer & Sohn). The Deutsche Chemische Gesellschaft has recently issued in pamphlet form the interesting and exhaustive lecture upon the aniline colors derived from coal tar, delivered before the Society by Dr. Caro on the 22d of June, 1891.

Annuaire Géologique Universelle: Revue de Géologie et Paléontologie, by Dr. L. Carez and H. Douvillé. The 4th fascicle of volume viii, year 1891, has been issued.

Geological and Solar Climates: Their Causes and Variations: A Thesis; by Marsden Manson, C.E., University of California. 49 pp., 12mo, May, 1893.

## APPENDIX.

## ART. XLV.—Restoration of Coryphodon; by O. C. MARSH. (With Plates V and VI.)

THE genus *Coryphodon*, established by Owen in 1846, is of great importance alike to geologists and paleontologists. It represents a remarkable group of large ungulate mammals now known to have lived both in America and Europe during early Eocene time. The remains are found in a distinct horizon, essentially the same in each continent. This horizon is so well marked that geologists may use it as a base for determining the age of other strata. The coryphodont mammals themselves are of special interest to anatomists, owing to the primitive characters shown in the skeleton. Perhaps their greatest importance lies in the fact, that these large hoofed mammals make their appearance suddenly in great numbers at the base of the Tertiary, without a hint as to their ancestral line, and with only diminutive generalized forms for their Mesozoic predecessors.

In Europe, various coryphodont remains, especially teeth, have been known under various names since the time of Cuvier, the first specimen, a molar tooth, having been found in 1807. All the remains since discovered there have likewise been fragmentary, and descriptions of them will be found in the works of Owen, Hébert, de Blainville, and more recent authors. A summary of the literature is given in the Palæontology of von Zittel, Volume IV, now in press.

The first specimen of *Coryphodon* discovered in America was found in 1871, near Evanston, Wyoming, by William Cleburne, while engaged as surveyor for the Union Pacific Railroad. He secured various remains, chiefly teeth and vertebræ, which were found together, and apparently belonged to a single individual. Some of these specimens he gave the same year to Prof. F. V. Hayden for transmission to Dr. Joseph Leidy, who failed to receive them. They were subsequently described by Prof. E D. Cope under the new generic names Bathmodon and Loxolophodon.\* Portions of the same skeleton, including both teeth and vertebræ, were later given to the writer by Mr. Cleburne, and with them the above statement of the discovery and disposition of the specimens found. Prof. Cope, in 1872, gave the name *Metalophodon* to a specimen from another locality in Wyoming, and subsequently (1873-1875), in several papers, and under the above generic names, described various remains from Wyoming and New Mexico. He also gave figures of a molar tooth, the hind foot, and a skull, all of which he referred to his genus *Bathmodon*.

\* Proc. Amer. Philos. Soc., vol. xii, pp. 417 and 420, 1872.

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In the meantime, the writer had been investigating remains of the same group from Wyoming and New Mexico, including portions of the original specimen found by Mr. Cleburne, and other material of much interest. It was soon ascertained (1) that all these remains were apparently identical with those of the genus Coryphodon, Owen, as described and figured by him and Hébert ;\* and (2) that the geological horizon of these fossils was essentially the same both in America and Europe. An investigation was made of the skull, and especially of its brain-cavity, the latter indicating a brain of very inferior type. The feet proved to be of a primitive form, the manus and pes each having five, very short, functional digits. The remains studied belonged to a new family, named by the writer the Coryphodontidae. These and other results were brought together in a paper entitled "On some Characters of the genus Coryphodon, Owen," and in it were given figures of the skull and the brain cavity of a new species, Coryphodon hamatus. This paper was published separately, April 15, 1876, and subsequently appeared in this Journal, vol. xi, p. 425, May, 1876.

Subsequent to the publication of these determinations by the writer, Prof. Cope admitted, in several papers, the reference of these remains to the genus *Coryphodon*, and the identity of the horizons in this country and Europe in which they were found, but without referring to the above article on the subject. He likewise described in detail, and figured, in 1877, what he considered a brain-cast of *Coryphodon*, but again without any reference to the paper in which, the year before, the writer had given accurate figures of the brain-cast of that genus. In the specimen described by Prof. Cope, the cribriform plates of the brain-case were apparently wanting, so that in the cast figured the olfactory lobes appear to extend far forward, thus giving a wrong idea of the original brain.<sup>+</sup>

In the same year, 1877, the writer published a second article under the title, "Principal Characters of the *Coryphodontida*," in which he gave more in detail a description of the skull and brain-cast of *Coryphodon*, with a figure, and also the main facts in regard to the skeleton. The feet of this genus, before practically unknown, were described and figured, and especially compared with those of *Dinoceras*, which were also represented for comparison.<sup>‡</sup> In Plate V of the present article, the original figures of the feet of *Coryphodon*, as given by the writer in 1877, are repeated. The original figure, also, of the

\* British Fossil Mammals and Birds, p. 299, 1846; and Annales des Sciences Naturelles, tome vi, p. 87, 1856.

+ Proc. Amer. Philos. Soc., vol. xvi, p. 616, plates i-ii, 1877. See also Amer. Naturalist, vol. xi, p. 312, and p. 375, 1877.

t This Journal, vol. xiv, p. 81, plate iv, July, 1877.

skull and the brain-cast, given by the writer first in 1876, and again in 1877, is repeated below, figure 1.

In another publication (this Journal, vol. xiv, p. 354, 1877), the writer defined more fully the horizon in the lower Eocene in which the *Coryphodontidæ* had been found in this country, and named the deposits the Coryphodon beds.

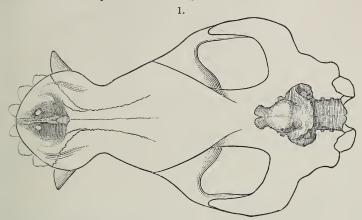


Figure 1.—Outline of skull and brain-cavity of *Coryphodon hamatus*, Marsh; top view. About one-fifth natural size.

The most important publication of Prof. Cope on the Coryphodontidæ will be found in Volume IV of the Wheeler Survey, published in 1877. The remains of a number of different forms, mainly from New Mexico, are described and figured, and the relations of the group to some allied mammals are discussed. In the following year, Prof. Owen published again on Coryphodon, in the Annals and Magazine of Natural History (vol. ii, p. 216, 1878), giving figures of some American forms. In various papers, Prof. Cope subsequently referred to the Coryphodontide, naming several supposed species and two genera, Manteodon and Ectacodon, but adding little of importance to what was already known of the group. In his volume on "The Vertebrata of the Tertiary Formations of the West," 1884, he again discusses at length the Coryphodontidee, and gives a number of new figures. The historical part, pp. 513–517, is marred by many errors, characteristic examples of which may be seen in two footnotes, pp. 513 and 516. The statements there made are erroneous, as has already been shown in the present article.

In his monograph on the *Dinocerata*, 1884, the writer discussed the various relations of the *Coryphodontidæ* to the *Dinocerata*, giving figures of the skull and brain-cast, the upper and lower molar teeth, and the feet, of *Coryphodon* hamatus. The name *Amblydactyla* was substituted for *Amblypoda*, and *Coryphodontia* for *Pantodonta*, the names replaced both being essentially preoccupied. Two recent papers by Mr. Charles Earle, on the *Coryphodontidæ*, are of interest.\* He treats of the teeth of this group, especially of their variations and homologies, and gives figures of some of the most characteristic forms. He also discusses at length the various American species named, and decides "that the large number of species which have been founded by Prof. Cope should be greatly reduced; and that in many cases his species are to be considered merely varieties, and that often these varieties are merely individual variations in the same species due to age and sex."

In a joint paper by Prof. H. F. Osborn and Dr. J. L. Wortman, which appears in the Bulletin of the American Museum, p. 81, 1892, the former discusses this group briefly, especially some specimens recently collected in the Wind River region by Dr. Wortman, and gives two figures of the feet of *Coryphodon*. In this paper, p. 118; the family *Coryphodon-tidæ*, established by the writer in 1876, is credited to Prof. Cope, but with no reference as authority, while the preoccupied names *Pantodonta* and *Amblypoda* are also used in place of *Coryphodontia* and *Amblydactyla*.

In discussing the foot structure of Coryphodon (p. 121), Prof. Osborn makes some very emphatic statements, which are important if true, but he gives no facts to support them, and there is good evidence that he is in error. One statement is as follows: "the positions of the fore and hind feet of Coryphodon were absolutely different, the fore foot was digitigrade like that of the Elephant, and the hind foot was plantigrade like that of the Bear." These positions are shown in his figures, which afford no evidence to support the statement, especially in regard to the hind foot. Again, in giving the characters of the feet, Prof. Osborn adds to what was already known, that the "second metacarpal" has a vertical ectocuneiform facet; a statement likewise open to question. Another assertion (p. 122) nearly as strange is, that in "The figure of the pes of Coryphodon given by Marsh . . . . the astragalus is represented as covering the entire upper surface of the cuboid." A reference to the figure in question (Plate V, fig. 2) will, however, show this statement, also, to be wrong, as the calcaneum covers about half the cuboid. This fact was clearly stated in the text when the figure was first published. The "unique caudal appendage" described by Prof. Osborn (p. 120), and the suggestion in regard to its use, do not require special notice here. The above points will be discussed later in the present article.

\*Science, vol. xx, p. 7, 1892; and Bull. Amer. Mus., vol. iv, p. 149, 1892.

## Restoration of Coryphodon hamatus.

After the above brief review of the more important literature relating to the coryphodont mammals found in America, the main object of the present article, the restoration of one species of *Coryphodon*, may be considered. In Plate VI, this restoration is given, one-twelfth natural size. The position shown was chosen after careful consideration, and is believed to represent fairly one naturally assumed by the animal in life, when standing at rest. The figure represents a fully adult individual of one of the largest species of the genus, which, when alive, was nearly six feet in length, and about three feet in height.

The basis of this restoration is the type specimen of *Corypholon hamatus*, and this was supplemented by other remains which appeared to be specifically identical. A large number of such specimens were available, some of them in excellent preservation. For parts of the skeleton where such remains were wanting, specimens from nearly allied forms were used, but no serious error can thus result. In these remains, the caudal vertebræ were seldom preserved in good condition, and although a sufficient number of such specimens from different individuals were at hand, the exact number in the present species could not be determined, and hence the vertebræ of the tail are left in outline.

No clavicles are represented in the restoration, and no evidence of their existence has been found by the writer in the many remains investigated. The specimens described by Prof. Cope as clavicles of *Coryphodon* probably do not pertain to that genus. A bone very similar in shape to the supposed clavicles was figured by him as the fifth metatarsal, in the first diagram he published of the hind foot of *Coryphodon*. The same figure has three phalanges in the first digit, and the ectocuneiform supported mainly by the astragalus; features not seen elsewhere by the writer.

#### The feet of Coryphodon.

The structure and position of the feet of *Coryphodon*, as represented in the restoration, require some consideration in this connection, in view of differing opinions on these points. The fore feet of *Coryphodon* were first figured and described by the writer, and on Plate V, figure 1, is the original cut then published. This figure was made from a well-preserved specimen in which both fore feet were present, and nearly in position when found. They were carefully kept in the matrix until prepared for the drawing, and hence the accuracy of the figure cannot well be questioned. The fore feet represented

### O. C. Marsh-Restoration of Coryphodon.

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in the present restoration are constructed mainly from the same specimen, and the position given in the original figure has been essentially retained. The small size of the restoration does not permit as accurate an exhibition of the structure of the feet as could be desired, but the main features are clearly shown. In this species, the pyramidal bone (cuneiform) touches the fifth metacarpal, and helps to support it, as in *Dinoceras*, as already shown by the writer. This is the rule in adult individuals of *Coryphodon*, but in young specimens, the metacarpal facet on the pyramidal may be indistinct or even wanting, as is sometimes the case with weathered specimens.

The hind feet of *Coryphodon* were investigated by the writer at the same time as the fore feet, and figure 2, Plate V, of the left pes was published with figure 1, and is believed to be equally accurate. Being a front view, it does not fully show the relations to each other of the astragalus, calcaneum, and cuboid, but the other elements are clearly exhibited. The position first given to the figure is retained in the restoration after a careful investigation of the whole posterior limbs in a number of well-preserved specimens. These differ considerably among themselves, but the essential structure is identical in all. The feet bones of some of these specimens are very perfect, and their relations to each other cannot well be misinterpreted.

The accompanying Plate V gives together the left fore and hind feet of Coryphodon, Dinoceras, and Elephas, all seen from in front. The feet of the three genera as exhibited have many points in common, and their positions during life were probably nearly the same. The feet of Coryphodon are the oldest in point of time, but those of the elephant are in some respects of a more primitive type. Those of *Dinoceras* are much nearer to Coryphodon in their general structure, but the points of resemblance need not be enumerated here. The elephant, as well known, has all the toes of each foot enclosed in a common integument, but is really digitigrade. In Dinoceras, the terminal phalanges are much larger, showing that they themselves bore a greater weight, the digits being undoubtedly free, although a pad may have helped to support the foot. In Coryphodon, the digits were still more elongate, and the terminal phalanges proportionately larger and broader, somewhat like those of the rhinoceros, indicating that they were covered with hoofs that supported the feet. This would agree with the position given them in the restoration, which coincides with the anatomical structure of the entire hind limb.

Yale University, New Haven, Conn., September 22, 1893.



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## [THIRD SERIES.]

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## ART. XLVI.—On New England and the Upper Mississippi basin in the Glacial period; by JAMES D. DANA.

SINCE the publication, in this Journal, of Prof. G. F. Wright's paper on the Unity of the Glacial epoch, nearly a year since,\* this subject has been much discussed in the scientific journals of the country, and with some interesting developments besides those within the purpose of the writers.

*First.* It has been shown that there are good working geologists on each side of the question.

Secondly. It has been made manifest that the advocates of unity are mainly the geologists that have investigated eastern glacial regions in the country, and especially New England, while the advocates of two Glacial epochs are chiefly those whose glacial studies have been in more western regions.

The writer, who has thus far taken no part in the recent discussion, here states that he has found in his geological explorations, which have been extensive over New England, the State of Maine excepted, no facts that require for their explanation an appeal to two glacial epochs, and none that has even suggested the idea.

Thirdly. The presentation of arguments on the side of unity has been moderate in tone and free from dogmatism. Among geologists on the other side, great confidence in the obvious facts has given occasion to expressions almost of accomplished triumph for the two-epoch theory.

\* Volume xliv, page 351.

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, No. 275.-Nov., 1893.

Fourthly. Among the prominent glacial investigators, one has been on both sides of the question. Having studied glacial phenomena long and faithfully in New England, Warren Upham explained the facts which he had observed on the theory of one advancing and retreating glacier, and found evidence of its terminal moraine and another halt moraine in the islands south of New England and on part of the adjoining main land. But after some years of study in Minnesota and the neighboring States and over the region northward through Manitoba, he adopted the theory of two glacial epochs. Returning again to New England and revising the facts there presented, he was led back to his former opinion, as he has announced in his recent papers. Since no geologist in America is better acquainted with the facts on the two sides, or more faithful and earnest in glacial investigation, these changes in his conclusions have special interest.

*Fifthly.* As the above review of facts makes manifest, the division among geologists on the question, and the differences in intensity of opinion, are to a large extent geographical.

The cause of this sectional divergence in views deserves consideration. The writer has come to the conclusion that the cause is largely *meteorological*: that the geological differences in opinion are a consequence not only of differences in observed facts in the west as compared with those of the east, but back of these, in meteorological differences in the two regions during the Glacial period.

At the present time the glaciated areas of eastern and central North America differ widely in hygrometric conditions. For New England and three-fourths of the State of New York the mean annual precipitation, according to Schott's maps, varies from 38 to 42 inches—a broad coast region, nearly half the breadth of New England, excepted over which it amounts in some parts to 50 inches; while for Wisconsin, it varies from 32 to 38 inches, and for the larger part of Minnesota, from 20 to 32 inches. North of New England in British America east of Hudson's Bay the annual precipitation is from 32 to 20 inches; but to the west of this region over Manitoba and beyond, it is 20 to 10 inches.

Here is a large present difference between the eastern and western regions, affecting snow-falls as well as rain-falls.

Now in the Glacial period, this eastern region would not only have had the same great advantage as now of proximity to the Atlantic Ocean, but also that of greater height than now. The evidence appears to be conclusive that along the Atlantic side of the continent from southern New England northward, as well as on the Pacific side, the continent stood much above its present level, and that the elevation was the culmination of that which was in progress during the closing part of the Tertiary era,—as urged by Prof. Upham. However much the surface of the great medial valley of the continent was raised, it cannot be reasonably questioned that the border mountain regions experienced the greater amount of elevation. Hence, with the mountain condensers on the east so much increased in altitude and extent, the differences between the eastern and interior regions as to precipitation would have been greatly augmented, to the advantage of the eastern region.

Further, the Glacial period was probably a time of greater precipitation than now, as well as of greater cold. Some have said, of greater precipitation, and not of greater cold; but the former of these two statements has general acceptance. If the surface waters of the Atlantic basin were warmer than now owing to a rise of land along a belt from southeast to northwest through Iceland as part of the general rise on the American and European sides—this would account for greater precipitation on the borders of the ocean, and especially over its western border, the American.

But leaving this source of increased precipitation out of consideration, it is plain that in the Glacial period the difference in amount of precipitation over the high eastern border made into a lofty ice plateau by the accumulation of snow and ice, and over the broad medial belt from Wisconsin and Minnesota northwestward, should have been much greater than it is now. Moreover, this central valley of North America would have had something of the existing disadvantage of a relatively warm summer temperature. At the present time, in July, a mean temperature of 70° F. extends beyond the latitude of Lake Winnipeg even to 56° N., and this is 10° in latitude, or nearly 700 miles, farther north than the position of the same heat-line over New England.

The advantages for ice-making of eastern over central North America were, therefore, very great, both as regards temperature and precipitation. When the conditions over the interior were sufficient to produce a small annual gain of ice, those over New England would have been making a very large annual gain. A small gain continued for many scores of centuries would make finally a great thickness of ice. But with the conditions over the interior near the critical point, a small unfavorable meteorological change if long continued, might carry off the ice for scores or hundreds of miles from a southern limit, with proportionate floods from the melting, while the eastern border was all the time gaining in ice, or was making only a short retreat.

The actual facts correspond with these views. The distance in the Upper Mississippi basin between the farthest southern limit of the ice and the line of the great moraine, or that of the so-called "second Glacial epoch," is over 500 miles; but to the eastward it narrows through Indiana, Ohio, Pennsylvania and New Jersey; and in New England a corresponding moraine interval cannot be certainly made out, and nothing exists that could not be better explained by reference to short retreats in a single glacier.

I leave the subject here for the consideration of geologists of the east and west. The cause appealed to explains at least why the geologists of the east and west are divided on the subject; and, also, why the grand display of terminal and retreat moraines characterizing the west, produces there the stronger opinions and the stronger expressions of opinions; and why also a complete survey of the facts will probably lead to a general agreement in favor of a single Glacial epoch only.

#### ART. XLVII.—On the Use of the Name "Catskill"; by JOHN J. STEVENSON.

Two years ago, the writer\* urged that the series of beds included within the Catskill and Chemung periods, should be grouped into one period, the Chemung, with three epochs, the Portage, the Chemung and the Catskill. Since that time Prof. Hall<sup>+</sup> has presented in detail the results of his later studies in the Catskill region, and Mr. N. H. Dartont has published a brief synopsis of work done by him for Prof. Hall in the same region. These papers supplement and confirm the previous notices of work done by Prof. Hall, as given by him§ from time to time in his official reports and elsewhere. In closing his paper, Mr. Darton suggests that "Catskill" be applied to the Upper Devonian as the name for the whole

\* Stevenson, The Chemung and Catskill (Upper Devonian) on the eastern side of the Appalachian basin. Vice-President's address before Amer. Assoc. Adv. Sci., vol. xl.

Hall, Bulletin Geol. Soc. of Amer., vol. iv, p. 8. Unfortunately only a reference to the paper is given with a brief statement respecting the discussion. The paper has not been published.

t This Journal, vol. xlv, 203-209.
S Hall, 28th Ann. Rep. of Regents on the State Museum, 1876, p. 15; Science, 1880, p. 290; Fifth Ann. Rep. of State Geologist, Assembly Doc. No. 105, 1886, p. 11. In this last the true relation of the Oneonta sandstone to the underlying Unrilter and the completion Computer Science and Science and Science Computer Science and Science Computer Science and Science and Science Computer Science and Science and Science and Science Computer Science and Science Computer Science and Science and Science and Science and Science Computer Science and Science a Hamilton and the overlying Chemung was stated and illustrated by a section.

period and that its use as the name of an epoch be discarded; this, in view of the new light thrown upon the subject by his paper. Mr. Darton has presented the conditions in the Catskill Mountains with great clearness and he has increased our stock of knowledge by the addition of details which fill up the gap for a portion of the southern border of New York, but the writer cannot see that any light has been shed upon the general problem of relations, which was not shining when the Address, already referred to, was prepared two years ago.

The making of names for local groups of rocks, if one wish to employ them, is simple enough; they may refer to some physical character, to the distribution of some fossil or to the locality itself. But to find a name for a vast formation is far from simple. The problem is to give some definitive appellation to a series of rocks covering or underlying many thousands of square miles, showing variations in lithologic characters and in thickness, in the distribution or even in type of animal or vegetable life. A name based wholly on paleontological grounds would be misleading; equally so would be one similarly based on lithologic characters. Evidently the only recourse is a geographical term referring to some locality, where one may find as nearly as may be, an average of all conditions shown in the areas available for study. No name should be given until after careful comparisons, that a wrong typical locality be not selected.

A single instance may be mentioned as illustrating the difficulty. The term "Umbral," applied by H. D. Rogers to the upper division of the Lower Carboniferous, being unacceptable, that group received from the 2d Geological Survey of Pennsylvania the name of Mauch Chunk Red Shale. This name answers well for the northeast corner of Pennsylvania, in the vicinity of the anthracite region, but it is found less and less applicable as one recedes from that region toward the southwest and southwardly along the easterly outcrop line; for sandstones, limestones and shales of different types are found; soon the limestones become important; eventually in the Virginias they predominate and the Mauch Chunk shales become an insignificant feature of this group, which represents the Chester and St. Louis, with part at least of the Keokuk of the Mississippi valley. Long ago, W. B. Rogers gave to this series the name of Greenbrier Group; on Greenbrier River of West Virginia the shales of northeastern Pennsylvania and the limestones of southwestern Pennsylvania are found developed to their greatest extent. This naming proves to be defensible on paleontological grounds as well-in almost every instance, careful stratigraphical and careful paleontological work come out closely in accord.

This case is very similar to that in hand. The problem is to give a name to the series of rocks between two sufficiently well defined limits, the Hamilton below and the Pocono above. The series in all its parts is practically persistent for fully six hundred miles along its easterly outcrop, from within a few miles of the Tennessee border through Virginia, Maryland, Pennsylvania and New York into the Catskill Mountains. Sections taken at short intervals show remarkable resemblance in detail, remarkable uniformity in the more important beds until within a short distance of the New York line, where the lithologic features hitherto characterizing only the highest members of the sections extend lower and lower until, in the Catskill Mountain region, they become almost equally characteristic of the lowest members. As the writer has shown for northern Pennsylvania along the State line by comparison of sections made by White, Ashburner and Sherwood and, as was shown by Hall and now also by Darton for southern New York, the same condition is observed in coming eastward toward the Catskill region. Recognizing this condition, but seeming to regard its discovery as new, Mr. Darton says :

"As the Catskill in its type region comprises Portage and Chemung, my proposition now is to discontinue the use of Catskill as a coördinate formation term and use the term Catskill group to include the Portage and Chemung formations, the latter extending to the base of the Lower Carboniferous. I believe the Chemung and Portage are formations distinctly separable over a wide area, but Chemung and "Catskill" as formations are only separable by a lithologic distinction, which progressively varies several thousand feet in stratigraphic position in the extension of the beds across southern New York."\*

This is now no mere strife about words; possibly were the name to be given *de novo*, the case might be different. But this is no beginning; the three groups, Portage, Chemung and Catskill have been recognized for forty years; they are recognizable as separate in an immense area, compared to which the Catskill Mountain region of New York is utterly insignificant. A lithologic distinction between Chemung and Catskill was not the basis on which the groups were separated in the typical locality of the latter, which is Susquehanna County of Pennsylvania<sup>+</sup> and no such distinction can be used with safety. That feature, however, was used in other localities, by Vanuxem himself as well as by other observers, in order to determine equivalence. This test led to Prof. Hall's placing of the Lower Chemung near Blossburg, Pennsylvania, into the Old Red Sandstone and therefore to regard the

\* Darton, loc. cit., p. 209.

† Vanuxem in Assembly Doc. No. 50, 1840, p. 381.

Holoptychius beds of Tioga County, Penn., as Catskill, whereas they lie but little above the Lower Chemung Conglomerate (Allegrippus of White), which, in Susquehanna County of Pennsylvania is at 1000 feet below the Montrose sandstone (Honesdale Sandstone of White), while in south central Pennsylvania along the easterly outcrop, the bed is fully 2000 feet below the Montrose sandstone. And the use of this lithologic test has been the cause of confusion and annoyance ever since.

The objections to the use of the name Catskill for the whole series are so strong as to render it certainly unwise if not altogether wrong; and they apply equally to the proposed disuse of the term to distinguish a subordinate formation.

That the Catskill Mountain region is not the typical area of the Catskill Group has been mentioned. It was there that Mather\* found his "Catskill Mountain Series," which included all the rocks of the Catskill region from the Lower Carboniferous Sandstone of H. D Rogers down to the bottom of the Marcellus, so that it comprehended the Hamilton, Chemung and Catskill as well as part of the Pocono. Vanuxeni<sup>+</sup> used the term "Catskill Group" in his final report to designate the summit rocks of the Devonian, the group to which he had given the name of Montrose sandstone in the fourth annual report.<sup>‡</sup> The distribution of the group as given in the final report differs little from that given in the annual report, but in the former the Oneonta sandstone is taken as the equivalent of the Montrose sandstone. The series was taken to be the same with the Old Red Sandstone of Prof. Halls which rests in the Chemung Group.

In spite of Vanuxem's error in the final report, that of identifying the Oneonta with the Montrose sandstone, it is doubtful whether any geological term has ever been applied to a better defined group than that made by Vanuxem in the fourth annual report, to which he gave the name of Catskill in his final report. The Montrose sandstone is a thoroughly well marked horizon, obscure only in the exceedingly restricted area of southern New York: it is traceable without difficulty in the sections along the eastern outcrop from northeastern Pennsylvania to many miles beyond New River in Virginia. Its variations in northern Pennsylvania westward are well shown in the sections obtained by I. C. White and in southern Pennsylvania westward in the sections obtained by Stevenson.

The Catskill of Vanuxem is distinct also in its history; its distribution is very different from that of the Chemung; it is

<sup>\*</sup> Mather, Assembly Doc., No. 150, 1841, pp 77-82.
† Vanuxem, Geology of New York, Part III, 1842, p. 12.
‡ Vanuxem, Assembly Doc., No. 50, 1840, p. 381.
§ Hall, Assembly Doc, No. 50, 1840, p. 452.

local. In southern Pennsylvania near the Maryland line its whole thickness of 3700 feet disappears within less than 60 miles westward from the eastern outcrop; in northern Pennsylvania it has practically disappeared before Blossburg in Tioga County has been reached; in southern New York, it should not reach beyond Chemung County. It must not be understood that this means that red rocks disappear; red rocks occur far below the Montrose at many places, so that rocks of "the Catskill type," as Ashburner termed them, appear at many localities west from the line of Catskill disappearance. The Chemung extends far to the west beyond the last traces of the Catskill and is easily recognized in western Pennsylvania and in Ohio.

The Catskill is as well defined as any group in the Devonian column; it is impossible, therefore, to discard the name as one designating a subordinate division of a series, the essential unity of which appears now to be conceded as fully as is the unity of the Hamilton or Niagara. The question still remains, however, does this Catskill portion so present the characters of the whole series as to justify the application of its name to the whole Upper Devonian period?

It is impossible to answer this question in the affirmative, for were the name so employed, it would give an erroneous impression respecting the conditions prevailing in by far the greater part of the Appalachian basin during most of the immense period represented by the Portage, Chemung and Catskill. It must be remembered that the Catskill Mountain region is not the typical area of the group which Vanuxem named "Catskill." The Catskill Mountain region, far from being the typical area of anything, has always been the area of doubt and dispute. Mather's too hasty gathering in of the red beds and Vanuxem's error respecting the relation of the Oneonta to his Montrose sandstone produced uncertainty for more than a third of a century and led to error in adjacent regions. The work in Pennsylvania did much to prepare the way for reconciliation of the facts which seemed to be at variance; but Prof. Hall's recognition of the relations of the Oneonta\* sandstone removed the mystery and made everything distinct.

He has shown that the Oneonta sandstone, instead of resting on the Chemung, is the base on which it rests, is, in fact practically, the eastward prolongation of the Portage. Mr. Darton's section from Broome County of New York eastward shows the same thing.

\* Hall, Fifth Ann. Report of State Geologist, Assembly Doc., No. 105, 1886, p. 11.

The constancy of the conditions within the Catskill Mountain area from the very beginning of the Upper Devonian made the relations of its rocks to those of other regions very perplexing. As Prof. Hall has shown, even before the close of the Hamilton, the conditions became unfavorable to animal and vegetable life and favorable to the formation of red beds; and these conditions, with rare interruptions, continued until the end of the Devonian. But as one recedes from the area of the Catskills, he finds that these conditions did not begin alike early everywhere\* and that the horizon at which red rocks become a marked feature, varies stratigraphically not less than 3000 feet; and the upper limit of animal life varies even to nearly 4000 feet, there being localities where some molluscan forms were able to sustain themselves amid the red beds at the very top of the section.

But this was no hap-hazard variation. The writer has shown that the conditions beginning so early in the Catskills of New York, spread toward the south and west slowly but steadily until at the close of the Devonian, they prevailed along the easterly outcrop to beyond the New River in Virginia and westward to the limits already given as those of the Catskill. The characteristic fossil of the Oneonta sandstone (Portage) in New York is the *Amphigenia*, commonly thought to be a freshwater form. As the conditions favorable to the existence of this mollusc extended, the geographical distribution must have become greater, so that there was no reason for surprise when, in 1881, the writer discovered that form near the summit of the Montrose sandstone in southwestern Pennsylvania, several thousand feet above the Portage, its horizon in the Catskills.

But these conditions spread very slowly; Mr. Darton's section from Broome County eastward in New York exhibits the changes observed previously in northern Pennsylvania by I. C. White and in southern Pennsylvania by Stevenson. So slowly did they spread, that for a very long period, lasting almost to the end of the Chemung, as limited above by Vanuxem, they had reached southwestward to barely 75 miles within Pennsylvania and westward but little further-an utterly insignificant area when we remember that the whole series has been examined along the easterly outcrop for 500 miles further southwestwardly and that, by means of the oil-borings and the successive anticlinals, the section is familiar to the southwestern limit of Pennsylvania; while the tracing along the northern line of Pennsylvania and the southern line of New York is sufficiently simple. Southwardly in Pennsylvania, one comes quickly to sections showing fossiliferous beds in the

\* Stevenson, loc. cit.

lower portion; each succeeding section in that direction shows the fossiliferous portion extending higher and higher, until in Huntingdon County, the whole mass below the Montrose sandstone, 4,675 feet thick, is more or less fossiliferous—the fossils being most abundant in beds near the top of the column. In southern Virginia, however, the change is more noteworthy, for there within Roanoke County, the writer in 1890 found Chemung forms far up in what is unquestionably the Catskill. Going westwardly, one finds the matter equally clear, the fossiliferous beds occurring higher and higher, while the whole mass diminishes in thickness; so that before western Pennsylvania has been reached Chemung fossils are present at the top of the section, the Montrose or Catskill having thinned out and disappeared.

So then, the "Catskill condition" existed within a very circumscribed area until the close of the Chemung epoch; but for some reason, the area was enlarged greatly during the Catskill. Red beds, it is true, had made their appearance at many localities long before that time, but, for the most part, they are insignificant features in the sections. It is sufficiently clear that to apply the name Catskill to the whole series of rocks would be to apply a term which would be misleading, as it refers to a locality exhibiting characteristics wholly or almost wholly absent from most or all of the section in nine-tenths of the area in which the series can be studied within the Appalachian region.

Of course, there are objections to the use of the term "Chemung" for the whole series; not much of the Catskill portion is present in the immediate region where the Chemung was studied by Hall in 1839. But undoubtedly there is a remnant of that group there, so that representatives of all three divisions of the series can be gathered under the name. The only objections to the use of the name are such as apply to the use of any geographical term; but the reasons favoring its use far outweigh any objections which may be offered.

In probably nine-tenths of the area in which this series is exposed within the Appalachian basin, the Chemung, that portion below the Montrose or Catskill of Vanuxem, is the important portion of the series; it is the persistent portion, with certain beds which are traceable directly over almost the whole region outside of the Catskill Mountain area; whereas the Catskill is not the persistent portion, occupying as it does only the long trough rudely parallel to the Blue Ridge from southern New York to very near the Tennessee line, as already defined. More than that; the fauna, termed Chemung by Hall in New York is typical of the whole section below the Montrose sandstone and in Virginia passes even into that portion of the section. Catskill is simply epochal but "Chemung" carries with it the conception of those physical and biological characteristics which mark the great closing period of the Devonian.

Chemung, therefore, and not Catskill is the epoch whose name should be applied to designate the whole group, while Catskill must be retained in its original signification only.

University of the City of New York.

## ART. XLVIII. -- The Finite Elastic Stress-Strain Function; by GEO. F. BECKER.

Hooke's Law.—The law proposed by Hooke to account for the results of experiments on elastic bodies is equivalent to :---Strain is proportionate to the load, or the stress initially applied to an unstrained mass. The law which passes under Hooke's name is equivalent to :- Strain is proportional to the final stress required to hold a strained mass in equilibrium.\* It is now universally acknowledged that either law is applicable only to strains so small that their squares are negligible. There are excellent reasons for this limitation. Each law implies that finite external forces may bring about infinite densities or infinite distortions, while all known facts point to the conclusion that infinite strains result only from the action of infinite forces. When the scope of the law is confined to minute strains, Hooke's own law and that known as his are easily shown to lead to identical results; and the meaning is then simply that the stress-strain curve is a continuous one cutting the axes of no stress and of no strain at an angle whose tangent is finite. Hooke's law in my opinion rests entirely upon experiment, nor does it seem to me conceivable that any process of pure reason "should reveal the character of the dependence of the geometrical changes produced in a body on the forces acting upon its elements."+

Purpose of this paper.-So far as I know no attempt has been made since the middle of the last century to determine the character of the stress-strain curve for the case of finite stress.<sup>+</sup> I have been unable to find even an analysis of a simple finite traction and it seems that the subject has fallen into neglect, for this analysis is not so devoid of interest as to be deliberately ignored, simple though it is.

\* Compare Bull. Geol. Soc. Amer., vol. iv, 1893, p. 38, + Saint-Venant in his edition of Clebsch. p. 39.

J. Riccati. in 1747, a brief account of whose speculation is given in Todhunter's history of elasticity, proposed a substitute for Hooke's law.

In the first part of this paper finite stress and finite strain will be examined from a purely kinematical point of view; then the notion of an ideal isotropic solid will be introduced and the attempt will be made to show that there is but one function which will satisfy the kinematical conditions consistently with the definition. This definition will then be compared with the results of experiment and substantially justified.

In the second part of the paper the vibrations of sonorous bodies will be treated as finite and it will be shown that the hypothesis of perfect isochronism, or perfect constancy of pitch, leads to the same law as before, while Hooke's law would involve sensible changes of pitch during the subsidence of the amplitude of vibrations.

Analysis of shearing stress.—Let  $\Re$ ,  $\Re$  and  $\mathfrak{T}$  be the resultant normal and tangential stresses at any point. Then if  $N_1$ ,  $N_2$  and  $N_3$  are the so-called principal stresses and  $\lambda$ ,  $\mu$ ,  $\nu$  the direction cosines of a plane, there are two stress quadrics established by Cauchy which may be written

$$\begin{aligned} \Re^2 &= N_1^2 \lambda^2 + N_2^2 \mu^2 + N_3^2 \nu^2, \\ \Re &= N_1 \lambda^2 + N_2 \mu^2 + N_3 \nu^2. \end{aligned}$$

Since also  $\mathfrak{T}^2 = \mathfrak{R}^2 - \mathfrak{N}^2$ ,

 $\mathfrak{T}^{2} = (\mathbf{N}_{1} - \mathbf{N}_{2})^{2} \lambda^{2} \mu^{2} + (\mathbf{N}_{1} - \mathbf{N}_{3})^{2} \lambda^{2} \nu^{2} + (\mathbf{N}_{2} - \mathbf{N}_{3})^{2} \mu^{2} \nu^{2};$ 

and these formulas include the case of finite stresses as well as of infinitesimal ones.

In the special case of a plane stress in the xy plane,  $N_s = 0$ and  $\nu = 0$ , and the formulas become

$$\begin{split} \mathfrak{N}^2 &= \mathrm{N_1}^2 \lambda^2 + \mathrm{N_2}^2 \mu^2,\\ \mathfrak{N} &= \mathrm{N_1} \lambda^2 + \mathrm{N_2} \mu^2,\\ \mathfrak{T}^2 &= (\mathrm{N_1} - \mathrm{N_2})^2 \lambda^2 \mu^2. \end{split}$$

In the particular case of a shear (or a *pure* shear) there are two sets of planes on which the stresses are purely tangential, for otherwise there could be no planes of zero distortion. On these planes  $\Re = 0$ , and if the corresponding value of  $\lambda/\mu$  is  $\alpha$ ,

$$-N_{\alpha} = N_{\alpha} / \alpha.$$

If this particular quantity is called Q/3, one may write the equations of stress in a shear for any plane in the form

$$\begin{split} \mathfrak{N}^2 &= \frac{Q^2}{9} \Big( \mu^2 \alpha^2 + \frac{\lambda^2}{\alpha^2} \Big), \\ \mathfrak{N} &= \frac{Q}{3} \Big( \mu^2 \alpha - \frac{\lambda^2}{\alpha} \Big), \\ \mathfrak{T}^2 &= \frac{Q^2}{9} \Big( \alpha + \frac{1}{\alpha} \Big)^2 \lambda^2 \mu^2. \end{split}$$

For the axes of the shear the tangential stress must vanish, so that  $\lambda$  or  $\mu$  must become zero, and therefore the axes of x and y are the shear axes. If  $\Re_x$  and  $\Re_y$  are the normal axial stresses, one then has

$$-\mathfrak{N}_{\mathfrak{s}}\alpha=\mathfrak{N}_{\mathfrak{s}}/\alpha=Q/3.$$

A physical interpretation must now be given to the quantity  $\alpha$ . In a finite shearing strain of ratio  $\alpha$ , it is easy to see that the normal to the planes of no distortion makes an angle with the contractile axis of shear the cotangent of which is  $\alpha$ . If the tensile axis of the shear is the axis of y, and the contractile axis coincides with x, this cotangent is  $\lambda/\mu$ . Hence in the preceding formulas  $\alpha$  is simply the ratio of shear.

In a shear of ratio  $\alpha$  with a tensile axis in the direction of oy, minus  $\Re_x \alpha$  is the negative stress acting in the direction of the x axis into the area  $\alpha$  on which it acts. It is therefore the load or initial stress acting as a pressure in this direction. Similarly  $\Re_y/\alpha$  is the total load or initial stress acting as a tension or positively in the direction oy. Hence a simple finite shearing strain must result from the action of two equal loads or initial stresses of opposite signs at right angles to one another the common value of the loads being in the terms employed Q/3.\*

It is now easy to pass to a simple traction in the direction of oy since the principle of superposition is applicable to this case. Imagine two equal shears in planes at right angles to one another combined by their tensile axes in the direction oy, and let the component forces each have the value Q/3. To this system add a system of dilational forces acting positively and equally in all directions with an intensity Q/3. Then the sum of the forces acting in the direction of oy is Q and the sum of forces acting at right angles to oy is zero.

Inversely a simple finite load or initial stress of value Q is resoluble into two shears and a dilation, each axial component of each elementary initial stress being exactly one-third of the total load. Thus the partition of force in a finite traction is exactly the same as it is well known to be in an infinitesimal traction, provided that the stress is regarded as initial and not final.<sup>+</sup>

\* This proposition I have also deduced directly from the conditions of equilibrium in Bull. Geol. Soc. Amer., vol. iv, 1893, page 36. It may not be amiss here to mention one or two properties of the stresses in a shear which are not essential to the demonstration in view. The equation of the shear ellipse may be written in polar coördinates  $1/r^2 = a^2\mu^2 + a^{-2}\lambda^2$ . Hence the resultant load on any plane whatever is  $\Re r = \pm Q/3$ . The final tangential stress is well known to be maximum for planes making angles of  $45^{\circ}$  with the axes; but it is easy to prove that the tangential load,  $\Im r$ , is maximum for the planes of no distortion. These are also the planes of maximum tangential strain. Rupture by shearing is determined by maximum tangential *load*, not stress.

+ Thomson and Tait, Nat. Phil., section 682.

## 340 G. F. Becker-Finite Elastic Stress-Strain Function.

Application to system of forces.—Without any knowledge of the relations between stress and strain, the foregoing analysis can be applied to developing corresponding systems of stress and strain. Let a unit cube of an elastic substance presenting equal resistance in all directions be subjected to axial loads P, Q, R. Suppose these forces to produce respectively dilations of ratios  $h_1, h_2, h_3$  and shears of ratios p, q, r. Then the following table shows the effects of each axial force on each axial dimension of the cube in any pure strain.

Active force	Р	Q	R
Axis of strain	x y z	x y z	x y z
Dilation Shear Shear	$egin{array}{cccc} h_{_1} & h_{_1} & h_{_1} \ p & 1/p & 1 \ p & 1 & 1/p \end{array}$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Grouping the forces and the strains by axes, it is easy to see that the components may be arranged as in the following table, which exhibits the compound strains in comparison with the compound loads which cause them, though without in any way indicating the functional relation between any force and the corresponding strain.

Pure Strains.

Axes	. 20	y	z
Dilation	$h_{1}h_{2}h_{3}$	$h_{1}h_{2}h_{3}$	$h_{_1}h_{_2}h_{_2}$
Shear	$\frac{p^2}{qr}$	$\frac{qr}{p^2}$	1
Shear	1	$\frac{pq}{q^{2}}$	$\frac{r^2}{pq}$
Products	$\frac{h_1h_2h_3p^2}{arr}$	$\frac{h_1h_3h_3q^2}{m^2}$	$\frac{h_1h_2h_3r^2}{m\alpha}$

#### Loads or Initial Stresses.

Axes	x	y	2
Dilation	$\frac{P+Q+R}{3}$	$\frac{P+Q+R}{3}$	$\frac{P+Q+R}{3}$
Shear	$\frac{Q+R-2P}{3}$	$\frac{Q+R-2P}{3}$	· 0
Shear	0	$\frac{P+Q-2R}{3}$	$-\frac{P+Q-2R}{3}$
Sums	P	Q	R

In many cases it is convenient to abbreviate the strain products. Thus if one writes  $h_1h_2h_3=h$ ,  $qr/p^2=a$  and  $pq/r^2=\beta$ , the product are h/a,  $ha\beta$  and  $h/\beta$ .

Inferences from the table.—It is at once evident that the load sums correspond to the products of the strain ratios, and that zero force answers to unit strain ratios. There are also several reciprocal relations which are not unworthy of attention. If R=0 and Q=-P, the strain reduces to a pure shear. But the positive force, say Q, would by itself produce a dilation  $h_2$ , while the negative force, minus P, would produce cubical compression of ratio  $h_1 < 1$ . Now a shear is by definition undilatational and therefore, in this case,  $h_1h_2=1$ . Hence equal initial stresses of opposite signs produce dilatations of reciprocal ratios. The same two forces acting singly would each produce two shears while their combination produces but Q would contract lines parallel to oz in the ratio 1/qone. while minus P would elongate the same lines in the ratio p/1. Since the combination leaves these lines unaltered, p/q=1. Hence equal loads of opposite signs produce shears of reciprocal ratios. It is easy to show by similar reasoning that equal loads of opposite signs must produce pure distortions and extensions of reciprocal ratios.

Strain as a function of load —One may at will regard strains as functions of load or of final stress; but there seem to be sufficient reasons for selecting load rather than final stress as the variable. To obtain equations giving results applicable to different substances, the equations must contain constants characteristic of the material as well as forces measured in an arbitrary unit. In other words the forces must be measured in terms of the resistance which any particular substance presents. Now these resistances should be determined for some strain common to all substances for forces of a given intensity. The only such strain is zero strain corresponding to zero force. Hence initial stresses or loads are more conveniently taken as independent variables.\*

### Argument based on small strains.

*Physical hypothesis.*—In the foregoing no relation has been assumed connecting stress and strain. The stresses and strains corresponding to one another have been enumerated, but the manner of correspondence has not been touched upon. One may now at least imagine a homogeneous elastic substance of such a character as to offer equal resistance to distortion in

\* When the strains are infinitesimal, it is easy to see that load and final stress differ from one another by an infinitesimal fraction of either.

every direction and equal resistance to dilation in every direction. The two resistances may also be supposed independent of one another—for this is a more general case than that of dependence. The resistance finally may be supposed continuous and everywhere of the same order as the strains.

In such an ideal isotropic substance it appears that the number of independent moduluses cannot exceed two; for a pure shear irrespective of its amount is the simplest conceivable distortion and no strain can be simpler than dilation, while to assume that either strain involved more than one modulus would be equivalent to supposing still simplier strains, each dependent upon one of the units of resistance. It is undoubtedly true that, unless the load-strain curve is a straight line, finite strains involve constants of which infinitesimal strains are independent; but these constants are mere coefficients and not moduluses: for the function being continuous must be developable by Taylor's Theorem, and the first term must contain the same variable as the succeeding terms, this variable being the force measured in terms of the moduluses. In this statement it must be understood that the moduluses are to be determined for vanishing strain.\*

One can determine the general form of the variable in terms of the resistances or moduluses for the ideal isotropic solid defined above. The load effecting dilation in simple traction, as was shown above, is exactly one third of the total load, or say Q/3; and if a is the unit of resistance to linear dilation, Q/3a is the quantity with which the linear dilation will vary. The components of the shearing stresses in the direction of the traction are each Q/3, and, if c is the unit of resistance to this

\* One sometimes sees the incompleteness of Hooke's law referred to in terms such as "Young's modulus must in reality be variable." This is a perfectly legitimate statement provided that Young's modulus is defined in accordance with it; but the mode of statement does not seem to me an expedient one to indicate the failure of linearity. Let  $\mu$  represent Young's modulus regarded as variable and F a force or a stress measured in arbitrary units. Then if y is the length of a unit cube when extended by a force, the law of extension may be written in the form  $y=1 + F/\mu$ . Now let M be the value of Young's modulus for zero strain, and therefore an absolute constant. Then, assuming the continuity of the functions, one may write  $\mu$  in terms of M thus,

$$\frac{1}{\mu} = \frac{1}{M} \phi\left(\frac{F}{M}\right) = \frac{1}{M} \left(1 + \frac{AF}{M} + \frac{BF^2}{M^2} + \dots\right).$$

But this gives

$$y = 1 + \frac{F}{M} + \frac{AF^2}{M^2} + \frac{BF^3}{M^3} + \dots$$

so that  $1/\mu$  merely stands for a development in terms of F/M. If therefore one defines Young's modulus as the tangent of the curve for vanishing strain, the fact of curvature is expressed by saying that powers of the force (in terms of Young's modulus) higher than the first enter into the complete expression for extension.

initial stress, the corresponding extension will vary with 2Q/3c. In simple extension all faces of the unit cube remain parallel to their original positions, and the principle of superposition is applicable throughout the strain. Hence the total variable may be written  $Q\left(\frac{1}{3a} + \frac{2}{3c}\right)$ . The intensity of Q will not affect the values of the constants a and c which indeed should be determined for vanishing strain as has been pointed out.

The quantities a and c have been intentionally denoted by unusual letters. In English treatises it is usual to indicate the modulus of cubical dilation by k and the modulus of distortion by n. With this nomenclature a=3k and c=2n. Using the abbreviation M for Young's modulus the variable then becomes

$$Q\left(\frac{1}{9k} + \frac{1}{3n}\right) = Q/M.$$

Since this is the form of the variable whether Q is finite or infinitesimal, the length of the strained cube according to the postulate of continuity must be developable in terms of Q/Mand cannot consist, for example, solely of a series of terms in powers of Q/9k plus a series of powers of Q/3n; in other words the general term of the development must be of the form  $A_m (Q/M)^m$  and not  $A_m (Q/9k)^m + B_m (Q/3n)^m$ .

Form of the functions.—If a is the ratio of shear produced by the traction Q in the ideal isotropic solid under discussion, a must be some continuous function of Q/3n. So too if h is the ratio of linear dilation, h is some continuous function of Q/9k. The length of the strained mass is  $a^2h$ , and this must be a continuous function of Q/M. If then f,  $\varphi$  and  $\psi$  are three unknown continuous functions, one may certainly write

$$\alpha^{2} = f\left(\frac{Q}{3n}\right); \qquad h = \varphi\left(\frac{Q}{9k}\right); \qquad \alpha^{2}h = \psi\left(\frac{Q}{M}\right). \tag{1}$$

It also follows from the definitions of  $\alpha$  and h that

$$1 = f(0);$$
  $1 = \phi(0);$   $1 = \psi(0).$  (2)

For the sake of brevity let  $Q/3n = \nu$  and Q/9k = x. Then  $\nu$ and z may be considered algebraically as independent of one another even if an invariable relation existed between n and k; for since in simple traction, the faces of the isotropic cube maintain their initial direction, the principle of superposition is applicable; and to put  $n = \infty$  or  $k = \infty$  is merely equivalent to considering only that part of a strain due respectively to

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compressibility or to pure distortion.\* Now the functions are related by the equation

$$f(\nu) \varphi(n) = \psi(\nu + n) \tag{3}$$

and if  $\nu$  and  $\varkappa$  are alternately equated to zero

$$f(\nu) = \psi(\nu)$$
 and  $\varphi(\varkappa) = \psi(\varkappa)$ .

Hence the three functions are identical in form<sup>+</sup> or (3) becomes  $f(\nu)f(\mu) = f(\mu + \nu).$  (4)

Developing the second member by Taylor's theorem and dividing by f(x) gives a value for  $f'(\nu)$ , viz:

$$f(\nu) = 1 + \frac{d f(\mu)}{f(\mu)d\mu} \cdot \nu + \dots$$

Since the two variables are algebraically independent, this equation must answer to McLaurin's Theorem, which implies that the expression containing x is constant, its value being say b. Then

$$\frac{df(n)}{f(n)} = bdn$$

Hence since f(0)=1

$$f(\varkappa) = \varepsilon^{b\kappa}$$

and since all three functions have the same form

$$f(\nu + \mu) = \epsilon^{b(\nu + \kappa)} = 1 + b Q/M + \dots$$

\* Compare Thomson and Tait Nat. Phil., section 179.

+ This proposition is vital to the whole demonstration. Another way of expressing it is as follows:---If the functions are continuous,

$$a^{2}h = 1 + A\left(\frac{Q}{3n} + \frac{Q}{9k}\right) + B\left(\frac{Q}{3n} + \frac{Q}{9k}\right)^{2} + \dots$$

where A, B, etc; are constant coefficients. Then since n and k are algebraically independent, or since the principle of superposition is applicable, the development of  $a^2$  is found by making h=1 and  $k=\infty$ . Thus

$$a^2 = 1 + \frac{AQ}{3n} + B\left(\frac{Q}{3n}\right)^2 + \dots$$

A, B, etc., retaining the same values as before. Consequently  $a^2$  is the same function of Q/3n that  $a^2h$  is of Q/M By equating a to unity and n to infinity, it appears that h also is of the same form as  $a^2h$ .

There is the closest connection between this method of dealing with the three functions and the principle, that, when an elastic mass is in equilibrium, any portion of it may be supposed to become infinitely rigid and incompressible without disturbing the equilibrium. For to suppose that in the development of  $a^2h$ ,  $k=\infty$  is equivalent to supposing a system of external forces equilibrating the forces Q/9k. This again is simply equivalent to assorting the applicability of the principle of superposition to the case of traction.

In pure elongation, unaccompanied by lateral contraction, it is easy to see that h=a and that a varies as Q/6n. In this case also 6n=9k because Poisson's ratio is zero. Hence without resorting to the extreme cases of infinite n or k, it appears that h is the same function of 9k that a is of 6n. This accords with the result reached in (5) without sufficing to prove that result.

Here b/M is the tangent of the load-strain curve for vanishing strain, and this by definition is 1/M, so that b=1.

It appears then that the equations sought for the loadstrain functions are

$$\alpha^{2} = \varepsilon^{Q/3n}; \qquad h = \varepsilon^{Q/9k}; \qquad \alpha^{2}h = \varepsilon^{Q/M}; \tag{5}$$

a result which can also be reached from (4) without the aid of Taylor's theorem.

Tests of the equations.—These equations seem to satisfy all the kinematical conditions deduced on preceding pages. It is evident that opposite loads of equal intensity give shears, dilations and extensions of reciprocal ratios and that the products of the strain ratios vary with the sums of the loads. It is also evident that infinite forces and such only will give infinite strains. A very important point is that these equations repre-sent a shear as held in equilibrium by the same force system whether this elementary strain is due to positve or negative forces. If any other quantity (not a mere power of Q or the sum of such powers), such as the final stress were substituted for the load Q, a pure shear would be represented as due to different force systems in positive and negative strains which would be a violation of the conditions of isotropy.\* One might suppose more than two independent moduluses to enter into the denominator of the exponent; but this again would violate the condition of isotropy by implying different resistances in different directions. Any change in the numerical coefficients of the moduluses would imply a different partition of the load between dilation and distortion, which is inadmis-It would be consistent with isotropy to suppose the sible. exponent of the form  $(Q/M)^{1+2c}$ ; but then, if c exceeds zero, the development of the function would contain no term in the first power of the variable and the postulate that strains and loads are to be of the same order would not be fulfilled. The reciprocal relations of load and strain would be satisfied and the loads would be of the same order as the strains, if one were to substitute a series of uneven powers of the variables for  $\nu$ Such series are for example the developments of  $\tan \nu$ and x.

\* Let a shearing strain be held in equilibrium by two loads, Q/3 and minus Q/3. If a second equal shear at right angles to the first is so combined with it that the tensile axes coincide, the entire tensile load is 2Q/3. If on the other hand the two shears are combined by their contractile axes, the total pressure is 2Q/3. In the first case the area of the deformed cube measured perpendicularly to the direction of the tension is  $1/a^2$ , and if Q' is the final stress,  $Q'/a^2 = 2Q/3$  or  $Q' = 2Qa^2/3$ . In the second case the area on which the pressure acts is  $a^2$  and if the stress is  $Q'', Q'' = -2Q/3a^2$ . Thus  $Q' = -Q'a^4$ . Hence equal final stresses of opposite signs cannot produce shears of reciprocal ratios in an isotropic solid. The same conclusion is manifestly true of any quantity excepting Q or an uneven power of Q or the sum of such uneven powers.

and tan x. In a case of this kind, however,  $\alpha^2 h$  would not be a function of  $Q/M = \nu + x$  excepting for infinitesimal strain; the exponent then taking the form of a series of terms  $A_m(\nu^m + x^m)$  instead of  $A_m(\nu + x)^m$ . Finally it is conceivable that the expanded function should contain in the higher terms moduluses not appearing in the first variable term; but this would be inconsistent with continuity. In short I have been unable to devise any change in the functions which does not conflict with the postulate of isotropy as defined or with some kinematical condition.

Abbreviation of proof.-In the foregoing the attempt has been made to take a broad view of the subject in hand lest some important relation might escape attention Merely to reach the equations (5) only the following steps seem to be essential. Exactly one-third of the external initial stress in a simple traction is employed in dilation, and of the remainder one half is employed in each of the two shears. An ideal isotropic homogeneous body is postulated as a material presenting equal resistance to strain in all directions, the two resistances to deformation and dilation being independent of one another; the strains moreover are to be of the same order as the loads, and continuous functions of them. In such a mass the simplest conceivable strains, shear and dilation, can each involve only a single unit of resistance or modulus. The principle of superposition is applicable to a simple traction applied axially to the unit cube however great the strain. It follows that the length of the strained unit cube is a function of Q/M.

Together these propositions and assumptions give (1) and without further assumptions the final equations sought (5) follow as a logical consequence.

Data from experiment.—No molecular theory of matter is essential to the mechanical definition of an isotropic substance. An isotropic homogeneous body is one a sphere of which behaves to external forces of given intensity and direction in the same way however the sphere may be turned about its center. There may be no real absolutely isotropic substance, and if there were such a material we could not ascertain the fact, because observations are always to some extent erroneous. It is substantially certain, however, that there are bodies which approach complete symmetry so closely that the divergence is insensible or uncertain. Experience therefore justifies the assumption of an isotropic substance as an approximation closely representing real matter.

All the more recent careful experiments, such as those of Amagat and of Voigt, indicate that Cauchy's hypothesis, leading for isotropic subtances to the relation 3k = 5n, is very far

from being fulfilled by all substances of sensibly symmetrical properties. This is substantially a demonstration that the molecular constitution of matter is very complex,\* but provided that the mass considered is very large relatively to the distances between molecules this complexity does not interfere with the hypothesis that pure shear and simple dilation can each be characterized by one constant only.

The continuity of the load-strain function both for loads of the same sign and from positive to negative loads is regarded as established by experiment for many substances; and equally well established is the conclusion that for small loads, load and strain are of the same order.<sup>+</sup> In other words Hooke's law is applicable to minute strains. Perfect elastic recovery is probably never realized, but it is generally granted that some substances approach this ideal under certain conditions so closely as to warrant speculation on the subject.

These results appear to justify the assumptions made in the paragraph headed "physical hypothesis" as representing the most important features of numerous real substances. On the other hand viscosity, plasticity and ductility have been entirely ignored; so that the results are applicable only to a part of the phenomena of real matter.

Stress-strain function.—It is perfectly easy to pass from the load-strain function to the stress-strain function for the ideal solid under discussion. The area of the extended cube is its volume divided by its length or  $h^{\circ}/\alpha^{\circ}h$ . Hence if Q' is the stress, or force per unit area,  $Q'h^{\circ}/\alpha^{\circ} = Q$ . Therefore the stress-strain function is

$$(\alpha^2 h)^{a^2/h^2} = \varepsilon^{Q'/M}$$

an equation which though explicit in respect to stress and very compact is not very manageable. If one writes  $a^2h = y$  and h/a = x, the first member of this equation becomes  $y^{1/x^2}$ . Here x and y are the coördinates of the corner of the strained cube.

Verbal statement of law.—If one writes  $a^2h-1=f$ , the last of equations (5) gives

$$df = (1+f) \, dQ/M$$

or the increment of strain is proportional to the increment of load and to the length of the strained mass. This is of course the "compound interest law" while Hooke's law answers to simple interest.

<sup>\*</sup>Compare Lord Kelvin's construction of the system of eight molecules in a substance not fulfilling Poisson's hypothesis in his Lectures on Molecular Dynamics.

<sup>&</sup>lt;sup>†</sup> Compare B. de Saint-Venant in his edition of Navier's Leçons, 1864, p. 14, and Lord Kelvin, Encyc. Brit., 9th ed., Art. Elasticity, Section 37.

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Curves of absolute movement.—Let  $\sigma$  be Poisson's ratio

or

$$\sigma = \frac{3k - 2n}{2(3k + 2n)}.$$

Let  $x_{o}y_{o}$  be the original positions of a particle in an unstrained bar, and let xy be their positions after the bar has been extended by a load Q. Then  $x=x_{o}h/a$  and  $y=y_{o}a^{2}h$ . It also follows from (5) that  $a^{e_{n}}=h^{e_{k}}$ , whence it may easily be shown that the path of the particle is represented by the extraordinarily simple equation\*

$$xy^{\sigma} = x_{\circ}y_{\circ}^{\sigma} \qquad (6)$$

If one defines Poisson's ratio as the ratio of lateral contraction to axial elongation, its expression is by definition

$$\sigma = -\frac{dx}{x} / \frac{dy}{y} = -\frac{ydx}{xdy};$$

and this, when integrated on the hypothesis that  $\sigma$  is a constant, gives (6). Thus for this ideal solid, the ratio of lateral contraction to linear elongation is independent of the previous strain.

The equation (6) gives results which are undeniably correct in three special cases. For an incompressible solid  $\sigma=1/2$ , and (6) becomes  $x^2y=$ constant, or the volume remains unchanged. For a compressible solid of infinite rigidity  $\sigma=-1$  and (6) becomes x/y=constant so that only radial motion is possible. For linear elongation unaccompanied by lateral extension  $\sigma=0$ , and (6) gives x=constant. $\dagger$ 

\* On Cauchy's hypothesis  $\sigma = 1/4$ , which, introduced into this equation, implies that the volume of the strained cube is the square root of its length.

+ It seems possible to arrive at the conclusion that  $\sigma$  is constant by discussion of these three cases Let e and -f be small axial increments of strain due to a small increment of traction applied to a mass already strained to any extent. Let it also be supposed that the moduluses are in general functions of the coördiuates, so that n and k are only limiting values for no strain. Then, by the ordinary analysis of a small strain (Thomson and Tait, section 682), one may at least write for an isotropic solid

$$e = P\left(\frac{1}{3n[1+f_1(x)]} + \frac{1}{9k[1+f_2(x)]}\right),$$
  
-f = P\left(\frac{1}{6n[1+f\_3(x)]} - \frac{1}{9k[1+f\_4(x)]}\right),

where f(x) is supposed to disappear with the strain. These values represent each element of the axial extension and each element of the lateral contraction as wholly independent. The value of  $\sigma$  is -f/e. Now for an incompressible substance, as mentioned in the text,  $\sigma=1/2$  and the formula gives

$$\sigma = \frac{1}{2} \cdot \frac{1 + f_1(x)}{1 + f_3(x)}, \text{ so that } f_1(x) = f_3(x).$$

Again for  $n = \infty$  only dilation is possible, or  $\sigma = -1$ , while the formula gives

# Argument from finite vibrations.

Sonorous vibrations finite.—In the foregoing pages the attempt has been made to show, that a certain definition of an isotropic solid in combination with purely kinematical propositions leads to a definite functional expression for the loadstrain curve. The definition of an isotropic solid is that usual except among elasticians who adhere to the rariconstant hypothesis, and it seems to be justified by experiments on extremely small strains. But the adoption of this definition for bodies under finite strain is, in a sense, exterpolation. It is therefore very desirable to consider the phenomena of such strains as cannot properly be considered infinitessimal.

It is usual to treat the strains of tuning forks and other sonorous bodies as so small that their squares may be neglected, and the constancy of pitch of a tuning fork executing vibrations of this amplitude has been employed by Sir George Stokes to extend the scope of Hooke's law to moving systems. It does not appear legitimate, however, to regard strongly excited sonorous bodies as only infinitesimally strained. Tuning forks sounding loud notes perform vibrations the amplitudes of which are sensible fractions of their length. Now it is certain that no elastician would undertake to give results for the strength of a bridge similarly strained, or in other words he would deny that such flexures were so small as to justify neglect of their squares.\*

Sonorous vibrations isochronous.—The vibrations of sonorous bodies seem to be perfectly isochronous, irrespective of the amplitude of vibration. Were this not the case, a tuningfork strongly excited would of course sound a different note from that which it would give when feebly excited. Neither

$$\sigma = -1 \cdot \frac{1 + f_2(x)}{1 + f_4(x)}$$
, so that  $f_2(x) = f_4(x)$ .

For pure elongation the lateral contraction is by definition zero, or  $\sigma\!=\!0,$  and the formula is

$$\sigma = \frac{f_3(x) - f_4(x)}{2[1 + f_2(x)] + 1 + f_1(4)}, \text{ whence } f_4(x) = f_3(x).$$

Hence all four functions of x are identical and  $\sigma$  reduces to its well known constant-form.—With  $\sigma$  as a constant equation (6) follows from the definition of  $\sigma$ ; and substituting  $a^{2}h = y/y_{\circ}$  and  $h/a = x/x_{\circ}$  gives  $a^{6n} = h^{9k}$ . If W = 6nlna one may then write

$$a = \epsilon^{W/6n}; \quad h = \epsilon^{W/9k}; \quad a^2 h = \epsilon^{W/M} = 1 + W/M + \ldots$$

Here experiment shows that W may be regarded either as load or stress; and reasoning indicates that it must be considered as load if M is determined for vanishing strain

\* It is scarcely necessary to point out that many of the uses to which springs are put, in watches for example, afford excellent evidence of the continuity of the load-strain function for finite distortions. musicians nor physicists have detected any such variation of pitch which, if sensible, would render music impossible. The fact that the most delicate and accurate microchronometrical instruments yet devised divide time by vibrations of forks, is an additional evidence that these are isochronous. Lord Kelvin has even suggested the vibrations of a spring in a vacuum as a standard of time almost certainly superior to the rotation of the earth, which is supposed to lose a few seconds in the course of a century.\*

It is therefore a reasonable hypothesis in the light of experiment that the load strain function is such as to permit of isochronous vibrations; but to justify this conclusion from an experimental point of view, it must also be shown that Hooke's law is incompatible with sensibly isochronous vibration. I shall therefore attempt to ascertain what load strain function fulfills the condition of perfect isochronism (barring changes of temperature) and then to make a quantitative comparison between the results of the law deduced and those derived from Hooke's law.

Application of moment of momenta.—If the cube circumscribed about the sphere of unit radius is stretched by opposing initial stresses and then set free, it will vibrate; and the plane through the center of inertia perpendicular to the direction of the stress will remain fixed. Each half of the mass will execute longitudinal vibrations like those of a rod of unit length fixed at one end, and it is known that the cross section of such a rod does not affect the period of vibration, because each fiber parallel to the direction of the external force will act like an independent rod. Hence attention may be confined to the unit cube whose edges coincide with the positive axes of coördinates, the origin of which is at the center of inertia of the entire mass.

The principle of the moment of momenta is applicable to one portion of the strain which this unit cube undergoes during vibration. The moment of a force in the xy plane relatively to the axis of oz, being its intensity into its distance from this axis, is the moment of the tangential component of the force and is independent of the radial force component. Now dilation is due to radial forces and neither pure dilation nor any strain involving dilation can be determined by discussion of the moments of external forces. Hence the principle of the moment of momenta applies only to the distortion of the unit cube. This law as applied to the xy plane consequently governs only the single shear in that plane.

The principle of the moment of momenta for the xy plane may be represented by the formula

\* Nat. Phil., sections 406 and 830.

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$$\frac{d}{dt} \sum m \left( x_1 \frac{dy_1}{dt} - y_1 \frac{dx_1}{dt} \right) = \sum \left( x_1 Y - y_1 X \right), \quad (7)$$

where the second member expresses the moments of the external forces, which are as usual measured per unit area, and  $x_1y_1$  are the coördinates of any point the mass of which is m.

Reduction of equation (7).—Let x and y represent the position of the corner of the strained cube; then the abscissa of the center of inertia of the surface on which the stress Y acts is x/2, and since Y is uniform,  $\Sigma x, Y = x Y/2$ . Similarly  $\Sigma y_{1}X = yX/2$ . Now xY and yX may also be regarded as the loads or initial stresses acting on the two surfaces of the mass parallel respectively to ox and oy, and in a shear these two loads are equal and opposite. Hence the second member of (7) reduces to x Y. It has been shown above that, if Q is an initial tractive load, Q/3 is the common value of the two equal and opposite loads producing one shear. But to obtain comparable results for shear dilation and extension, Q/3 must be measured in appropriate units of resistance. Since M is the unit of resistance appropriate to extension, the separate parts of the force must be multiplied by M and divided by resistances characteristic of the elementary strains. Now

$$\frac{M}{2n}\cdot\frac{Q}{3} + \frac{M}{2n}\cdot\frac{Q}{3} + \frac{M}{3k}\cdot\frac{Q}{3} = Q,$$

and it is evident that 2n/M is the unit in which Q/3 should be measured for the single shear.\* Thus the second member of (7) becomes MQ/6n.

This, then, is the value which the moment of the external forces assumes when these hold the strained unit cube in equilibrium. This unit cube forms an eighth part of the cube circumscribed about the sphere of unit radius. When the entire mass is considered, the sum of all the moments of the external forces is zero; since they are equal and opposite by pairs. If the entire mass thus strained is suddenly released and allowed to perform free vibrations, the sum of all the moments of momenta will of course remain zero. On the other hand the quantity MQ/6n will remain constant. For this load determines the limiting value of the strain during vibration and is independent of the particular phase of vibration, or of the time counted from the instant of release. It may be considered as the moment of the forces which the other parts of the entire material system exert upon the unit cube.

<sup>\*</sup> In this paper changes of temperature are expressly neglected. The changes of temperature produced by varying stress in a body performing vibrations of small amplitude can be allowed for by employing "kinetic" moduluses, which are a little greater than the ordinary "static" moduluses. Thomson and Tait, Nat. Phil, section 687.

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Turning now to the first member of (7), values of  $x_1$  and  $y_1$  appropriate to the case in hand must be substituted. Each point of the unit cube during shear moves on an equilateral hyperbola, so that if  $x_0$ ,  $y_0$  are the original coördinates of a point,  $x_1y_1 = x_0y_0$ . For the corner of the cube, whose coördinates are x and y, the path is xy = 1. Now  $x_1/x_0 = x$  and  $y_1/y_0 = y$  so that

$$x_1 dy_1 - y_1 dx_1 = x_0 y_0 (x dy - y dx)$$

If  $\psi$  is the area which the radius vector of the point x, y describes during strain, it is well known that  $2d\psi = xdy - ydx$  and, since in this case xy = 1, it is easy to see that

$$2d\psi = 2d \ln y$$

Since the quantities x and y refer to a single point, the sign of summation does not affect them, and the first member of (7) may be written

$$\frac{d^2 ln y}{dt^2} \Sigma_2 m x_{\circ} y_{\circ}$$

Here one may write for m,  $\rho dx_{o}dy_{o}$ , where  $\rho$  is the constant density of the body; and since the substance is uniform, summation may be performed by double integration between the limits unity and zero. This reduces the sum to  $\rho/2$ .

Value of  $\alpha$ . Equation (7) thus becomes

$$\frac{d^2 ln y}{dt^2} = \frac{2}{\rho} \cdot \frac{MQ}{6n}$$

the second member being constant. Counting time from the instant of release, or from the greatest strain, and integrating y between the limits  $y = \alpha$  and y = 1 gives

$$ln\alpha = \frac{MQ}{6n} \cdot \frac{t^2}{\rho}$$

It is now time to introduce the hypothesis that the vibrations are isochronous. It is a well known result of theory and experiment that a rod of unit length with one end fixed, executing its gravest longitudinal vibrations, performs one complete vibration of small amplitude in a time expressed by  $4\sqrt{\rho/M}$ . In the equation stated above t expresses the time of one-quarter of a complete vibration or the interval between the periods at which y = 1 and y = a. Hence for a small vibration, t as here defined is  $\sqrt{\rho/M}$ . If the vibrations are to be isochronous irrespective of amplitude, this must also be the value of t in a finite vibration. Hence at once

$$\alpha = \varepsilon^{Q/6n} = \varepsilon^{\psi},$$

the same result reached in (5).

This result may also be expressed geometrically. The quantity Q/6n is simply the area swept by the radius vector of the point  $x_{\circ} = 1$ ,  $y_{\circ} = 1$ . This area is also the integral of ydx from  $x = 1/\alpha$  to x = 1, or the integral of xdy from  $y = \alpha$  to y = 1. Thus  $\psi$  represents any one of three distinct areas. In terms of hyperbolic functions,  $\alpha = \sin \psi + \cos \psi$  and the amount of shear is  $2\sin \psi$ .

It appears then that isochronous vibrations imply that in pure shear the area swept by the radius vector of the corner of the cube, or  $ln\alpha$ , is simply proportional to the load. The law proposed by Hooke implies that the length  $\alpha - 1$  is proportional to the same load. The law commonly accepted as Hooke's makes  $\alpha - 1$  proportional to the final stress, or  $(\alpha - 1)/\alpha$ proportional to the load.

Value of h.—Knowing the value of a, the value of h can be found without resort to the extreme case  $n = \infty$ . In the case of pure elongation, unattended by lateral contraction, h = a and 9k = 6n. If a, and h, are the ratios for this case,

$$\alpha_{1} = \varepsilon^{Q/9k} ; h_{1} = \varepsilon^{Q/9k} ; \alpha_{1}^{2}h_{1} = \varepsilon^{Q/3k}$$

If three such elongations in the direction of the three axes are superimposed, the volume becomes

$$(\alpha_1^2 h_1)^3 = \varepsilon^{Q/k},$$

and this represents a case of pure dilation without distortion. Here however  $\alpha_1 = h_1$  and therefore the case of no distortion, irrespective of the value of n, is given by

$$h^{\scriptscriptstyle 9} = \varepsilon^{Q/k}$$

The values of  $\alpha$  and h derived from the hypothesis of isochronous vibrations when combined evidently give the same value of  $\alpha^2 h$  which was obtained from kinematical considerations and the definition of isotropy in equation (5).

Law of elastic force.—Let s be the distance of a particle on the upper surface of a vibrating cube from its original position or

$$s = \alpha^2 h - 1 = \varepsilon^{Q/M} - 1.$$

Then the elastic force per unit volume is minus Q, or

$$\rho \frac{d^2s}{dt^2} = -Q = -Mln(s+1) = -Ms + \frac{Ms^2}{2} - \dots$$

When the excursions of the particle from the position of no strain are very small, this becomes

$$\rho \frac{d^2s}{dt^2} = -Ms$$

a familiar equation leading to simple harmonic motion.

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Limitation of harmonic vibrations.—While the theory of harmonic vibrations is applicable to very small vibrations on any theory in which the load strain curve is represented as continuous and as making an angle with the axes whose tangent is finite, it appears to be inapplicable in all cases where the excursions are sufficient to display the curvature of the If the attraction toward the position of no strain in locus. the direction of oy is proportional to y-1, then in an isotropic mass there will also be an attraction in the direction of oxwhich will be proportional to 1-x. The path of the particle at the corner of a vibrating cube will therefore be the resultant of two harmonic motions whose phases necessarily differ by exactly by one-half of the period of vibration, however great and however different the amplitudes may be. This resultant is well known to be a straight line. Hence the theory precludes all displacements excepting those which are so small that the path of the corner of the cube may properly be regarded as rectilinear. It seems needless to insist that such cannot be the case for finite strains in general.

There is at least one elastic solid substance, vulcanized india rubber, which can be stretched to several times its normal length without taking a sensible permanent set. Now if the ideal elastic solid stretched to double its original length (or more) were allowed to vibrate, the hypothesis of simple harmonic vibration implies that this length would be reduced to zero (or less) in the opposite phase of the vibration, a manifest absurdity.

Variation of pitch by Hooke's taw.—It remains to be shown that if the commonly accepted law were applicable to finite strain, sonorous vibrations would be accompanied by changes of pitch which could scarcely have escaped detection by musicians and physicists. Experiments have shown that the elongation of steel piano wire may be pushed to 0.0115 before the limit of elasticity is reached.\* Since virtuosos not infrequently break strings in playing the piano, it is not unreasonable to assume that a one per cent elongation is not seldom attained. In simple longitudinal vibration the frequency of vibration is expressed by 1/4 of  $\sqrt{M/\rho}$ , and if according to Hooke's law, s = Q/M, where Q is the load, the number of vibrations, v, may be written

$$v = \frac{1}{4}\sqrt{\frac{Q}{s\rho}}$$
.

If, on the other hand, according to the theory of this paper, ln(1+s) = Q/M the number of vibrations, u, may be written

<sup>\*</sup> From experiments on English steel piano wire by Mr. D. McFarlane.

$$u = \frac{1}{4}\sqrt{\frac{Q}{\rho \ln(1+s)}}$$
 so that  $\frac{v}{u} = \sqrt{\frac{\ln(1+s)}{s}}$ .

If s = 0.01, this expression gives v/u = 400/401.

It would appear then that on the hypothesis of Hooke, a note due to longitudinal vibrations of about the pitch  $G_s$ would give a lower note when sounding fortissimo than when sounding pianissimo, and that the difference would be one vibration per second, or one in four hundred. But according to Weber's experiments experienced violin players distinguish musical intervals in melodic progressions no greater than 1000/1001, while simultaneous tones can be still more sharply discriminated.\* The value of s corresponding to v/u = 1000/1001 is only 0.004, and consequently strains reaching only about one-third of the elastic limit of piano wire should give sensible variations of tone during the subsidence of vibrations if Hooke's law were correct.

Longitudinal vibrations are not so frequently employed to produce notes as transverse vibrations. The quantity  $M/\rho$ enters also into the expression for the frequency of transverse vibrations though in a more complex manner. In the case of rods not stretched by external tension, the ratio v/u would take the same form as in the last paragraph. One theory of the tuning-fork represents it as a bar vibrating with two nodes, and therefore as comparable to a rod resting on two supports.

A pair of chronometrical tuning-forks could be adjusted to determine much smaller differences in the rate of vibration than 1000/1001; for the relative rate of the forks having been determined on a chronographic cylinder for a certain small amplitude, one fork could be more strongly excited than the other and a fresh comparison made. The only influences tending to detract from the delicacy of this method of determining whether change of amplitude alters pitch, would seem to be the difficulty of sustaining a constant amplitude and the difference of temperature in the two forks arising from the dissipative action of viscosity.

Conclusion.—The hypothesis that an elastic isotropic solid of constant temperature is such as to give absolutely isochronous longitudinal vibrations leads to the conclusion  $ln(\alpha^2 h) = Q/M$  without any apparent alternative. Comparison with the results of Hooke's law shows that, if this law were applicable to finite vibrations, easily sensible changes of pitch would occur during the subsidence of vibrations in strongly excited sonorous bodies.—The logarithmic law is the same deduced in the earlier part of the paper from the ordinary definition of the ideal elastic isotropic solid, based upon experiments on

\* Helmholtz, Tonempfindungen, page 491.

very small strains, in combination with purely kinematical considerations.—There can be no doubt that the law here proposed would simplify a great number of problems in the dynamics of the ether and of sound, as well as questions arising in engineering and in geology, because of the simple and plastic nature of the logarithmic function. In the present state of knowledge, the premises of the argument can scarcely be denied; whether the deductions have been logically made must be decided finally by better judges than myself.

Washington, D. C., July, 1893.

ART. XLIX. — On Powellite from a new Locality; by GEORGE A. KOENIG and LUCIUS L. HUBBARD, Michigan Mining School, Houghton.

THE material for this investigation was found in the 21st level of No. 8 shaft South Hecla Copper Mine, Houghton Co., Michigan, in the fall of 1892. It came into the possession of the authors through Mr. John T. Reader of the Tamarack mine.

Three small pieces were obtained, which had evidently resulted from the breaking up of a larger piece—altogether about 45 grams. In its present condition it appears homogeneous, that is to say, there is no other mineral associated with it except a trace of native copper. The finder states that the three pieces were lying in a cavity. The specimen, when examined with the lens, exhibits an irregular polysynthetic structure. Some of the aggregates terminate in a more or less distinct pyramid. Three of the small groups were detached for measurement. The signals were not very distinct, and the results, therefore, are only approximate.

Basal edge 49° 15'; pole edge 79° 59'.

The powder yields microscopic, positive and uniaxial images and the *tetragonal* symmetry may be assumed as fairly established. Mellville\* gives for powellite:

 $111 \land 1\overline{1}1 = 49^{\circ} 12; 111 \land 101 = 80^{\circ} 1'.$ 

Two cleavages were observed, one distinct and apparently parallel to 111, the other imperfect, parallel to 001. Hardness = 4.5. Spec. Gr. = 4.349. The color is pale bluish green; in patches it is deep olive- or asparagus-green. The luster is vitreous and unctuous. A thin section of the mineral under the microscope showed high double refraction (colors of the

\* This Journal, No. 242, p. 138, Febr., 1891.

third to fourth order), and dichroism ( $\alpha =$ blue,  $\gamma =$ green). Before the blowpipe the mineral is infusible, decrepitates, and in the closed tube gives no volatile products. With the fluxes, borax and microcosmic salt, the reactions are strongly indicative of molybdenum and faintly of tungsten. The salt of phosphorus bead in the inner flame being emerald green for molybdenum and blue for tungsten, it is evident that tungsten cannot be directly recognized when present in small quantity alongside of molybdenum, except in a modification of the green color. One mg. of the mineral being dissolved in 50<sup>mg</sup> of vitrified microcosmic salt and 0.8<sup>mg</sup> of MoO, (specially purified) in the same quantity of the salt, both treated thoroughly in the inner flame, exhibit very nearly the same color on cooling; it is noticed, however, that the bead containing the mineral is slightly fainter in intensity and of a slightly increased bluish green. Without such comparative test the examiner would not be aware of any difference. The fine powder dissolves readily in hydrochloric and nitric acids, making slightly yellow solutions in which an excess of ammonium hydrate produces but a very slight flocculent precipitate (Fe(HO), SiO). When the fine powder (0.1<sup>mg</sup>) is mixed with potassium-hydrogen sulphate, moistened with a drop of water, and the paste kneaded on the palm of the hand, it assumes a deep blue color, which intensifies at first upon breathing upon the material, but on continued breathing the color fades away and finally disappears altogether. The color may be brought back by heating the paste on plat.-foil and by again breathing upon it. (The latter part of this delicate reaction for Mo seems to be new). If  $1^{mg}$  of the mineral be dissolved in  $1^{cc}$  of conc. HCl and tin foil be added, the solution turns first green, then colorless and then carmine red. It is stated in all text books that acid molybdic solutions turn brown or brown red when treated with Zn or Sn. This is true for Zn but not for Sn. The ammoniacal solution precipitates with oxalic acid white CaC<sub>a</sub>O<sub>a</sub> and thus the mineral is proved to be essentially a calcium molybdate. The quantitative separation of the oxides of Mo and W is not possible by any of the published methods. The following two analyses were made by two independent methods.

In (I) Mo and W were precipitated by  $Hg_2(NO_3)_2$  and weighed as nearly white oxides. These were then subjected at a yellow heat to a current of dry air until no further volatilization was noticed. A small bluish green residue was left in the boat. In microcosmic salt this residue gave a bead purplish gray instead of blue. With borax the reaction for Mo was obtained. It was found by colorimetric trials that a mixture of oxides (specially purified)

of  $\begin{array}{c} WO_{s} & 1.7^{mg} \\ MoO_{s} & 0.3^{mg} \end{array}$  in S. Ph. 50<sup>mg</sup>

produced just such a nearly colorless bead as the above residue. Upon this proportion is based the percentage of WO, in analysis (I).

The results of analysis (II) are the most satisfactory of several trials. The methods followed are those of H. Rose and v. der Pfortden—precipitation of  $MoS_s$  in tartaric solution. It was found that the  $MoS_s$  after repeated solution and precipitation and final reduction to the metal would still leave a residue upon volatilization, which reacted in microcosmic salt like the one in (I).\* The sulphides were weighed and aliquot portions reduced to metal in a current of dry hydrogen, and from these weights of the metals the figures are deduced.

	I.	II.
MoO <sub>3</sub>	65.74	67.84
WO		1.65
CaO		27.30
MgO		·16
Fe <sub>2</sub> O <sub>3</sub>	undet.	•96
SiO <sub>2</sub>		1.52
Cu		trace
	97.65	99.43

The percentages of  $WO_s$  in (I) and (II) may be taken as a maximum and minimum respectively. Possibly the mean of the two is near the true percentage. In order to form a normal tungstate and molybdate we have

for (I)  $MoO_{3}$  65.74 require.... 25.56 CaO WO<sub>3</sub> 4.50 require.... 1.09 +0.76 26.65 for (II)  $MoO_{3}$  67.84 require.... 26.38 CaO WO<sub>3</sub> 1.65 require.... 0.40

#### 26.78 + 0.52

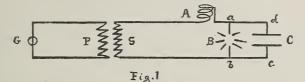
Analysis (II) with its plus of 0.52, and (I) with its plus of 0.76 of CaO are, neither of them, up to the theoretical requirement, but we do not know what role SiO<sub>2</sub> plays. The latter must be present as a silicate decomposable by HCl and NHO<sub>3</sub>, for these acids leave no residue when acting on the powder.

It may be questioned whether Melville was justified in speaking of his powellite as practically pure calcium molybdate, it showing over 10 per cent WO<sub>3</sub>. This name would properly go to the intermediate combinations of calcium tungstate and calcium molybdate. The pure molybdate awaits discovery and should then be given a new name.

\*This residue was found, by calculation, to contain an amount of W that could not exceed 0.984 per cent WO\_3.—L. L. H.

# ART. L.—On Increasing the Frequency of Electrical Oscillations; by A. H. PATTERSON and C. H. ARNOLD.

THE experiments of Hertz showed that the sparks from a transformer are complex and that only certain sparks, characterized by peculiar light and noise, are capable of awakening resonance in neighboring circuits. In fig. 1, G represents



a suitable alternator, P the primary, S the secondary of a transformer, B an air gap, C a suitable condenser. Each impulse of the generator G causes a corresponding impulse in the circuit S. If the condenser C is suitably charged, at each impulse of the generator sparks will oscillate across the airgap, B. The time of oscillation of one kind of sparks will be dependent upon the capacity and self induction in the circuit d, a, b, c, while the time of oscillation of another species of sparks will depend upon the self induction A and S and the capacity C. In general the transformer S serves as a choking coil, and the time of oscillations of the spark at B can be obtained from the expression  $t = 2\pi\sqrt{\text{LC}}$ , given by Lord Kelvin in a paper on the theory of transient currents, a paper in which, as it has been well said, Lord Kelvin has packed the whole theory of transient currents.

It is evident, therefore, that only those sparks which occur in a circuit of definite self induction and capacity can awaken sparks in a circuit of equal self induction and capacity. Hertz's work has seemed to illustrate the laws which Lord Kelvin and Maxwell have deduced from theory, and the commercial uses of alternating dynamo machines have enabled recent experimenters to show many well known phenomena on a much larger scale than was possible when the old form of transformer known as the Ruhmkorf coil was excited merely by batteries. There is danger, however, that in the successful attempts to increase the scale of representation of the remarkable efforts obtained by Professor Crookes the distinction between impulse and oscillation may become obscured.

An impulse is a sudden throb of a current which is produced by a change in electromotive force. A generator, for instance, giving 400 alternations of current per second will

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send 400 impulses through the outside circuit. If the well known relation  $\frac{R^*}{L} < \frac{4}{C}$  holds in that circuit a number of oscillations will follow each impulse. Among recent writers Mr. Tesla is especially vague on this point. For instance on page 40 of his little book of "Experiments," speaking of one of his dynamos he says, "It is capable of giving currents of a frequency of about 10,000 a second." Here and undoubtedly throughout the book he uses the expression frequency of a current for its frequency of impulse; but in his last lecture he says, in regard to reducing frequency, "This I may do by inserting a self induction coil in the path of the discharges or by augmenting the capacity of the condensers."\* Here he must use frequency of the currents for frequency of oscillation of current because the number of electric impulses per second given by the dynamo cannot be lowered by any arrangement of self induction and capacity, while the theory of transient currents shows that the frequency of oscillation can be reduced in either of the ways suggested in the passage just quoted. The same writer expresses himself in a vague manner on another point-the relation between the frequency of oscillation in the primary and that in the secondary of a transformer. It can be shown that the frequency of oscillation in the primary, in general, does not affect the electrical oscillations in the secondary--unless the circuits are in resonance. The body of the pilot spark as shown by photographic study is much greater than that of the spark due to any succeeding oscillation. The sparks due to the oscillations which follow the pilot spark decay rapidly according to the laws of transient currents in proportion to  $E^{-\frac{Rt}{2L}}$ , so that all oscillations except the first one in the primary have little effect upon a secondary circuit unless the two circuits are in resonance, which in general is not the case in the experiments shown by Mr. Tesla.

The number of impulses per second in a secondary coil is exactly the same as the number in the primary but the number of oscillations in the secondary may be greater or less than those in the primary. Electrical oscillations cannot be transformed in the same way as electric impulses. Although this statement is susceptible of mathematical proof, we have thought it desirable to study the transformation of electrical oscillations by the photographic method employed by Federsen, Lorenz, Trowbridge and others. The apparatus was that described by Prof. Trowbridge.<sup>+</sup> The arrangement of our apparatus is shown in fig. 1. G was an alternating dynamo, which gave a current of 26.5 amperes at 400 complete alternations per second through the primary P of a transformer the sec-

\* The Electrical World, vol. xxi, No. 22, p. 414. + Phil. Mag., Dec., 1891.

ondary of which S, had a resistance of 2000 ohms and a self induction of 47.64 Henrys. The number of turns of S was 23.700. A was a choking coil of 3200 ohms resistance and a self induction of 34.84 Henrys. B was a spark gap and C a condenser formed of metallic plates  $8 \times 10$  inches, which were immersed in castor oil at a distance of half an inch from each The capacity of the oil condenser was 6500 electroother. Since the circuits a, b, c, d and a, b, S A are static. units. two circuits through which electrical oscillations can surge and since they have very different values of L and C, formula (1)  $t = 2\pi_{\Lambda}/\text{LC}$  indicates that the frequency of oscillation in the one is quite different from that in the other. Since the oscillations of both circuits must vibrate between the terminals at B it would seem that the photographic image of the spark at B would be made up of these two sets of oscillations. Obtaining the value of t for the circuit a, b, c, d from eq. (1) we find it to be exactly equal to that obtained from a study of the photograph of the spark at B. There are, undoubtedly, oscillations also in the circuit a, b, S, A. The large capacity C and the great self induction of A and S however make the value of t in eq. 1 very large for this circuit. So large that in the case under consideration the oscillations are even fewer than the impulses of the generator in the circuit a, b, S, A. Indeed it is impossible to force oscillations through a comparatively small self induction without making t comparatively large.

Fig. 2 shows another arrangement of apparatus. A second transformer has been added, through the transformer of which

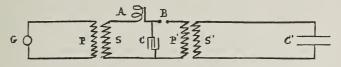


Fig.2

it has attempted to force the oscillations of the spark at B. The spark gap was placed in a very strong magnetic field. The transformer was a copy of that described by Mr. Tesla.\* The secondary S' of this transformer was wound in two parts with 260 turns in each part, the whole resistance being 24 ohms. The wire was heavily insulated with gutta percha and there was no iron core. The self induction did not exceed '001 Henry. Owing to the self induction of P' the time of oscillation in the circuit enclosing P', C, and B was large—a few thousandths of a second. If the circuit composed

\* Experiments with alternating currents of high frequency and high potential, pp. 15-17.

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of S' and C' had a product LC equal to that of the circuit P', C, B the time of oscillation in the two circuits would be the same : but since the products LC and L'C' in the two currents are quite different—the values of t are also different. The photographic study of the sparks bore out the truth of theoretical deductions and showed conclusively that electrical oscillations in a primary current in general do not give rise to a higher number of oscillations in a secondary circuit. If a higher number of oscillations occur in a secondary circuit than exist in a primary, there must be an air gap in this secondary circuit and a suitable arrangement of condensers and self induction. The oscillations which surge across such an air gap in the secondary in general have no relation to the oscillations across their gap in the primary circuit unless the circuits are in resonance. Our conclusion on this point is therefore this: the pilot spark of a primary circuit can give a series of impulses in a secondary-an increase of electromotive may result-which can The oscillaforce a spark across an air gap in this secondary. tions however of this last mentioned spark are not determined in general by the oscillations of the spark in the primary, and are dependent upon the arrangement of self induction and capacity in the secondary circuit.

In the course of our experiments to test the question of increasing the frequency of electrical oscillations we were led to examine the function of the magnetic field and the air blast in the transformation of electrical impulses. When the spark B, figures 1 and 2, occurs in a strong magnetic field and there are no condensers in the circuit it is instantly blown out with a sharp report. With comparatively small capacity connected with the spark terminals a torrent of sparks leap between the spark terminals. Without the magnetic field these sparks fill a globular space between the terminals. When the magnetic field is made, this spherical space is transformed into a plane of sparks, showing in a striking manner the Amperian law of repulsion and attraction of currents. The amount of light emitted by the passage of the sparks is also greatly increased by the passage of the sparks in the magnetic field; and it is interesting to observe the breaking away, so to speak, of the sparks from the surfaces of the terminals far from the actual points. The increase of light is doubtless due to the blowing out of the unidirectional fuzzy spark which if it is not blown out acts like a voltaic arc and prevents the condensers from becoming fully charged. When the condenser surface is increased to the proper limit, sparks of larger body take the place of the thread-like sparks, and the spreading out into a plane is no longer observed. Professor Boys from certain eye observations has concluded that a strong magnetic field has no effect upon the oscillations of a spark. We have tested this point by taking photographs of an oscillating spark both in and out

of a strong magnetic field and are able to substantiate his result; for no effect of the field was observed. The function of the magnetic field and the air blast therefore appears to reside in the blowing out of a species of voltaic arc which would tend to prevent the full charge, and the quick discharge of a condenser.

While we have dwelt in this paper principally upon the point of the difference between impulse and electrical oscillation and upon the possibility of transforming one and of the limits of transformation of the other, we are led also to speak of the importance of adjusting the rate of frequency of the impulses of the generator to the time of charging the condenser which is employed. It is evident that the rate of the generator should not be higher than the time taken to charge the condenser: for in that case the quantity of discharge would be less than that which might be obtained with a slower rate of alternation in the generator.\* For spectrum analysis we have found that a generator giving 400 alternations per second gave better results with various dielectrics than an alternator giving 1000 alternations per second.

Jefferson Physical Laboratory.

# ART. LI.—On the Geology and Petrography of Conanicut Island, R. I.; by L. V. PIRSSON.

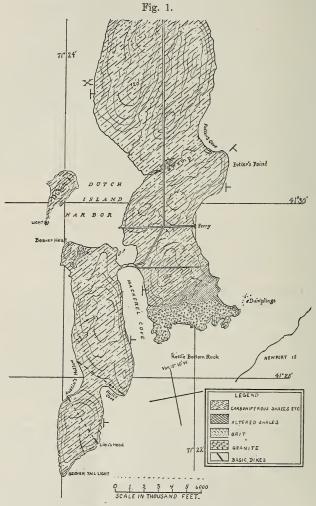
CONANICUT Island, lying in Narragansett Bay in Rhode Island and crossed by the meridian 71° 23' of west longitude and the parallel 41° 30' of north latitude, is about nine miles long in its greatest extent and nowhere much over a mile in breadth. As will be seen by reference to the map of fig. 1 it consists in reality of two portions, one large, the other much smaller, connected by a curving sand beach about an eighth of a mile long and nowhere much above a hundred yards in breadth.

The island consists in the main of extremely fissile soft shales, which weathering easily have determined the topography and given rise to smoothly rounded slopes and low hills. The highest point is about 135 feet above sea level. These smooth and undulating surfaces afford therefore no exposures of the underlying rocks and it is only along the shores where the constant gnawing of the waves has cut into the soft shales, making in places rugged shore lines, that

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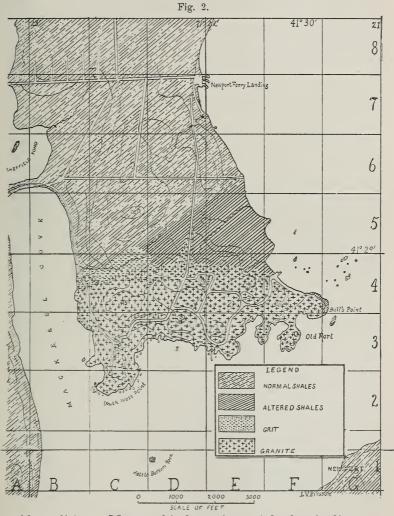
<sup>\*</sup> Indeed the rate of the alternator may be so rapid that a large condenser in the circuit can be made to appear of small capacity. And under these conditions the condenser will not serve to annul self induction. The time of the residual charges must also be taken into account. The charging of a condenser, therefore, by means of an alternator is far from a simple phenomenon.

the rocks can be studied. To this general character, however, the extreme southern end of the main portion affords a notable exception: at this point a stock of intruded granite and tough hornstone rocks resulting from the metamorphism of the shales afford by their superior resisting properties a group of low, rugged and rocky hills, precipitous water fronts and



outlying islets, which are known under the name of the Dumplings. This portion of the island has become a well known seaside resort and the hills are dotted with summer villas. A map of it is shown in fig. 2.

Everywhere on the island occur bowlders of the glacial drift, among which by far the most common rock is a coarse conglomerate containing rounded granitic and quartzose pebbles; furthermore this conglomerate is seen in the bowlders not only in normal condition but also at times evincing the fact that before removal it had suffered dynamic pressures resulting in a gneis-



soid condition. Masses of it from six to eight feet in diameter occur at times. Granite, gneiss and slates occur also as bowlders and pebbles in the drift. The island is covered with a fertile soil but is too narrow to give rise to any but inconsiderable drainages.

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*Historical.*—We are indebted, so far as I have been able to discover, to Jackson\* for the first map and geological description of Conanicut. He regards the shales forming the main portion of the island as of Carboniferous age and the granite as intrusive in nature and describes very clearly and correctly the metamorphoses suffered by sedimentaries by the intrusion of an igneous rock. He also gives a few dips and strikes that are in the main correct. The same views were also held by President Hitchcock.<sup>+</sup> It is to be noted that these observers correlated the granite and other rocks with the granite and rocks on Newport Neck adjacent. They were substantially the views of C. H. Hitchcock; and also of T. Sterry Hunt§ except slight variations as to the age of a portion of the sedimentary beds at Newport. Various papers have been published by different authors also on the Narragansett basin as a whole, treating the subject from various points of view. Since, however, in so far as Conanicut is concerned, they do not appear to be based on personal observation and the island is not directly named, they are not given here. For a list of them the reader is referred to a paper by T. N. Dale. This latter author in 1884¶ gives in a paper on the geology of the lower part of the basin, a pretty full account of Conanicut, based chiefly on a series of stratigraphical studies. He correlates the granite with that on Newport Neck and on stratigraphical grounds does not regard it as intrusive but as the lowest of his series and a metamorphic product. He describes the lithologic character of the various schists, shales, etc., and gives a large number of dips and strikes. Since, however, Dale, on Conanicut at least, mistook slaty cleavage for bedding, his conclusions, based as they are on largely mistaken stratigraphy, cannot be admitted. That this mistake was made, is evident, not alone from the given dips and strikes, but in the paper itself, where he several times mentions the shales as being "striped across the bedding." This striping is however the original bedding cut across by slaty cleavage; in many places on Conanicut the cleavage and bedding are parallel but generally not.

Geologically the sedimentary beds of Conanicut are of Carboniferous age, as is shown by their correlation with the coalbearing strata of the region. Moreover on the most western point of the main portion at X, fig. 1, fossil plants are found of Carboniferous species according to Dr. A. E. Foerste. In general these sedimentaries are made up of an extremely fissile shale or phyllite, varying in color from grayish green or

<sup>\*</sup> Geol. Surv. Rhode Island, 1840, pp. 89-92.

ł E. Hitchcock, Geol. Mass., 1841, pp. 537-552.

Geol. Is. Aquidneck, Proc. Am. Ass. Adv. Sci., 1860, pp. 119, 121, 126.

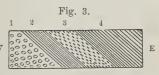
S Proc. Bost. Soc. Nat. Hist, vol. xiv, 1869. Proc. Bost. Soc. Nat. Hist., vol. xxii, p. 179, 1883.

This Journal, vol. xxvii, 1884, pp. 217-226, 282-291.

silver-gray to varieties dark chocolate to black in tone. The light varieties are well exposed along the eastern shore as at Potter's Point where the dark varieties also occur in thin beds. The darker varieties occur also along the shores of Mackerel Cove. Frequently the two are interbedded in extremely thin layers but an inch or so in thickness, which cut across at an angle by the planes of cleavage gives a peculiar ribboned appearance to the outcrops, this being well shown along the east shore of Mackerel Cove in B 5, fig. 2. The dark shales sometimes contain small garnets in vast numbers and sometimes staurolite, while the green shales do not as they are deficient or wholly wanting in lime as shown by the analysis given later. There are also at X, fig. 1, a few outcrops of a pudding stone or rather coarse conglomerate and also of some micaceous sandstones.

When we attempt, however, to unravel the stratigraphy of these beds we are met by great difficulties; as before said, there are no outcrops except at the shores; here however, with few exceptions, they are either exposures of the planes of slaty cleavage on which the strike of the beds may be seen but from which their dip cannot be determined, or of such a nature that neither strike nor dip can be told. In general, so far as can be made out, the strike of the beds on Conanicut is north and south and the dip east. Along the shore from the ferry to Potter's Point, the strike is nearly north and south-the dip cannot be safely told; at Potter's Point the strike changes with a short radius and runs out under the water in a northeast direction. At this point a large number of small faults with small displacements can be seen. Along the Beaver-tail portion of the island the strike is about north and south, the dip which varies considerably to the east. The same is true along the east shore of Mackerel Cove the dip varying from  $10^{\circ}$ - $30^{\circ}$ ; at a point nearly at the top of B 5 there is a small but excellent exposure which shows the beds bent into a half circle with radius of little more than a foot, the convex side to the east; this must have been an overfold and gives evidence of the great amount of distortion the beds have suffered. At X, fig. 1, an excellent exposure of the rocks

is found. A section at this point from the water's edge to the bank under which the rocks disappear is w given in fig. 3. The strike is north and south, the dip east. At this point along the shore the dip may be seen to have great variation. The cleavage is parallel to the bedding and the beds have



1 Conglomerate.

2 Black fissile shales.

3 Micaceous sandstone.

4 Shales.

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somewhat curved outcrops; they wedge out in places along the strike and are filled with veins and large lenticular masses of secondary quartz. The conglomerate of the given section contains quite large rounded pebbles in a fine grained cement; where its outcrop can be traced along the shore it is seen in places to have suffered severely from dynamo metamorphic processes, the pebbles are flattened, the cement becomes micaceous and transitions to gneiss or mica schist occur. It is strikingly similar in lithologic characters to the drift bowlders found over the lower part of the island and wholly different from the conglomeratic grit next to the granite on the east shore of Mackerel Cove in C 4.

The granite of Conanicut is coarse grained of a mixed gravish color on fresh exposures and it contains large often huge phenocrysts of orthoclase well distributed. These phenocrysts are of great importance in determining the relations of the granite and the grit in C 4. Petrographically the granite is described later. As will be seen by reference to the map, fig. 2, it forms the whole of the lower portion of the main part of the island. Its subaqueous limits can be pretty well defined by the sedimentaries on the west shore of Mackerel Cove; to the south by Kettlebottom Rock which is an outcrop of shale rising some eight feet above tide. Attempts were made to examine this rock closely but the heavy seas breaking on it prevented a landing; at a distance of some fifty yards it could be easily seen to be of shales and it is not probable that a drift mass could remain on a ledge in such an exposed position. On the Newport shore to the S.W. the shales recur again and the small island to the S.E. of Bull's Point in G 3 is composed as to its north part of altered sedimentaries and to the south of granite.

Evidences of intrusion.—That the granite is intrusive is best seen at Bull's Point where it is directly in contact with the sedimentary beds here altered to a dense hornstone-like rock. The granite is finer grained and more porphyritic; the contact between the two rocks is solid, specimens breaking across both as if one rock: it has sent out apophyses in the shape of dikes which cut into the sedimentary beds. Further to the eastward in E 4 the contact is buried, but at one point the granite and hornstone are but a few yards apart; here the granite is fine grained and aplitic in character, the hornstone extremely dense and tough. A short distance further westward between two little hills in E 4 there occurs an outcrop on the east side and near the bottom of the westward hill of a dark flinty rock, felsitic in appearance, characteristic of the contact facies of rapidly chilled highly siliceous magmas and which microscopically shows a crypto-crystalline groundmass

interspersed with quartz and feldspar often in micro-pegmatite intergrowth. This grows coarser in grain and a few yards to the south the granite outcrops again.

Also in D 5 occurs an apophysis which has been thrust out into the sedimentaries. Its outcrops occur along and in the road for a distance of some fifty feet or more and recent work on the road has thrown out some fresh material. This is a fine grained light reddish rock and microscopic examination shows it to be a most characteristic and typical micro-pegmatite. From this point farther to the westward there are no evidences of endomorphic contact in the granite; it is either covered or the rocks have suffered so from pressure and weathering that nothing certain can be deduced.

Exomorphic contact phenomena.—As will be seen by reference to the map, the region of the sedimentaries which has been chiefly affected by the intrusion of the granite is a roughly triangular mass lying in great part, in D 5 and E 5. It is not however the only place where exomorphic evidences of contact are shown. It may be said at this place that every transition can be found between unaltered shales and the most solid of hornstones in contact with the granite, but not however in any one place or exposure. Along the west shore of Mackerel Cove the shales although nearly normal are yet somewhat affected having a strongly knotted and speckled look, described by Dale\* as containing " thickly disseminated minute nodules of siderite." They often do indeed contain carbonates but also at other times small nests of intertwined white mica leaves, secondary quartz, chlorite, etc. It would appear at times as if they might have been pseudomorphs of some former mineral and the whole phenomenon is indeed strongly suggestive of contact metamorphism. In C 4 in the gully cut by the little brook and just west of the new road, green shales or phyllites are found which are very near the normal, the only alteration noticeable being a slight loss of the fissile character together with a somewhat gnarled appearance and the formation of small knotted points. In the N.W. corner of D 5 just south of Mr. Green's barn occurs a long outcrop extending towards the south. At the north end the shales although still retaining a fissile character are very much gnarled and toughened and as one proceeds southward they pass within two or three rods into compact hornstones. From this exposure it may be seen that the loss of the shaly character and transition into hornstone occurs within a very short distance.

Along the east shore in E 6 the transition is covered and the first outcrop after leaving the shales is a dense slaty rock of a

dark color and much jointed showing macroscopically only by color banding its sedimentary origin. Farther to the southward the rocks become more greenish or grayish green in color and more coarsely crystalline. In general it may be said that as we approach the granite the hornstones are more crystallized, harder, denser and break with a splintery fracture.

As previously noted the sedimentary beds are thin, vary in character and have a general N. and S. strike, consequently as one traverses the metamorphosed area in an E. and W. direction along the line of the granite there is considerable variation in the character and mineral constitution of the altered rocks as will be shown later. Another striking feature in the metamorphic character of these rocks is the presence of great quantities of fine veins of a yellowish color which traverse them in all directions, and which on microscopic examination are found to consist chiefly of tourmaline, of all minerals in the contact zone perhaps one of the most characteristic of the fumarole action of intrusive masses.

Grit.—Besides the conglomerate already mentioned as occurring at X and which is assumed as the lowest of the sedimentary series on the island there occurs another conglomerate rock or grit, exposed on the east shore of Mackerel Cove in close connection with the granite and evidently derived from it. It extends inland into C 4 as shown on the map: its outlines from a lack of good exposures are rather doubtful but probably as given. It differs widely from the first mentioned conglomerate in character in that it consists of fragmental granitic material; it is more of the nature of a grit consisting of quartz grains and fragments mixed with decayed feldspar material. Dale has characterized it as a "quartz clay aggregate." Its derivation chiefly from the granite both from its position and character of material seems quite clear. Moreover it contains fragments and even entire crystals of the large orthoclase phenocrysts which form so striking a character of the granite, their crystal form, broken or somewhat rounded. Its derivation from the granite would make it more recent than the adjoining sedimentaries and this is evinced by the fact that it contains fragments of shales. Some of these near the granite are slabs several feet in length whose long extension or strike is a little north of east and south of west, while they are standing nearly perpendicular, the strike of the shales to the north being N. and S. and the dip E. The granite adjoining though much weathered has evidently been strongly sheared and the whole appearance of this local mass of brecciated material is strongly suggestive of its being the result of pressure and shearing between the granite and the altered conglomerates, shales, etc., at this point.

Dikes.—The granite is cut through by aplite dikes in several places, an excellent example being a small one of but a few inches in width which cuts the exposed rock below and to the east of Mr. Clothier's house on Bull's Point, and which has been bent and faulted by later movements. Besides these which are in intimate connection with the granite there are two other dikes on the island, both on the Beavertail portion and cutting it and the strike of the beds transversely; see fig. They are not large, the one at Hull's Cove is the larger 1. and at this exposure from eight to ten feet wide. Its outcrop can be traced for some distance in a series of nearly buried bowlders.

The second one, a little south of the point known as Lion's Head is still narrower. Its western outcrop occurs on the south point of Austin's Hollow.

These dikes are of the lamprophyre rock known as minette or mica trap as will be shown later. They stand in close petrological relation to the granite and must be considered as of contemporaneous origin.

They have altered the adjacent shales, the one at Hull's Cove in particular having produced a rock similar in appearance to some of those formed in the contact zone of the granite as previously described

Orographic movements.-Besides the original folding of the Carboniferous series the island has suffered great dynamic pressures subsequent to the intrusion of the igneous rocks. The thrust has been in a general north and south direction. The granite has been crushed and dynamo-metamorphosed in places; planes of fracture extend through it generally in an E. and W. direction, often highly slickensided as in an excellent exposure at the gate to the grounds of Mr. J. Wharton in C 3. The aplite dikes in it have been bent and broken. The minette dikes on Beavertail have also been bent and folded and highly pressed; in places they have become quite schistose as at the south point of Austin's Hollow and the schistosity is perpendicular to the thrust. The sedimentaries have also suffered from these forces, steps in the shales running E. and W. being of frequent occurrence and the beds in other places have been fractured and bowed up as at X, the fractures and hollows from bending being now filled with veins and lenticular masses of secondary quartz.

General summary.-From the foregoing facts the following general statement may be deduced for the geology of Conanicut Island. That it is in the main made up of a series of Carboniferous strata thinly bedded with a conglomerate as the oldest member, which has been folded so that the beds have a general north and south strike and dip mostly to the eastward.

That there has been a later intrusion of granite which has necessarily metamorphosed the sedimentary strata and which has been accompanied by the injection of dikes petrologically related to the granite, and lastly the whole mass has suffered from dynamic forces acting in a general north and south direction, the result of orographic movement and which has also produced by shearing a mass of local grit.

Note.—The author desires at this point to express his thanks to Dr. A. E. Foerste who some years since made a brief study of the island and has kindly given the writer a short abstract of his notes made at that time. His outlining of the areas and of the dikes is essentially the same as that here given. From the presence of feldspar in the hornstones at one point he is inclined to regard them as composed partly of altered older basic eruptives, and the grit at Mackerel Cove he prefers to correlate with the basal conglomerate of the basin, though he regards it as derived from the granite. In other respects the views of the writer are believed to be in agreement with those expressed by Dr. Foerste.

#### Petrography.

Granite.—The Conanicut granite is a rather coarse grained rock, on fresh surfaces of a light reddish color due to the iron oxide developed in the feldspar. As remarked before it carries nearly everywhere huge phenocrysts of orthoclase, examples 5<sup>cm</sup> by 3<sup>cm</sup> in width and thickness being a very common size. It is therefore, strictly speaking, a granite porphyry, only on a much larger scale of size of phenocryst and grain of groundmass than usual. All of the main constituents may be determined by the eye, magnetite, titanite, oligoclase, orthoclase and quartz, also dark masses of chlorite which are the representatives of a former ferro-magnesian mineral.

Under the microscope are found in addition zircon, apatite, white mica and epidote, and it is seen that the rock even in the freshest examples has suffered severely from dynamic pressures; the quartzes show undulatory extinction, the feldspars are broken and filled with sericite. The large phenocrysts have also suffered in this way and the cracks are filled with secondary quartz and calcite. The ferro-magnesian mineral is no longer recognizable, its place is entirely taken by chlorite, often mixed with epidote. It is possible that hornblende as well as biotite was originally present, the epidote as an alteration product and the association with titanite rather favoring the idea.

With regard to the order of crystallization of the various components, the rock has in general been subjected to too much alteration of various kinds that obscure the structure to draw safe conclusions: in regard to the large phenocrysts, since they contain apatite, titanite, etc., it may be said that they are not the first products of crystallization while their more or less idiomorphic outlines indicate that they are older than the groundmass in which they lie. It is a striking fact that the rock never contains any phenocrysts of quartz and in this is unlike most peripheral facies, dike forms, etc., of granite porphyry. And it is probably true that while granites with large feldspar phenocrysts are not uncommon they rarely or never contain corresponding phenocrysts of quartz as might be expected from analogy with effusive forms—an indication that they have been formed under different conditions. The analysis of this granite yielded the results here presented.

SiO	71.23
SiO <sub>2</sub> TiO <sub>2</sub>	•21
$Al_2 O_3$	13.64
$\mathrm{Fe}_{2}^{2}\mathrm{O}_{3}^{3}$	1.70
FeO	1.00
MnO	.05
MgO	0.75
CaO	2.31
Na <sub>2</sub> O	3.55
K <sub>0</sub> Õ	3.79
H <sub>2</sub> O	1.72
-	
Total	99.95
Sp. G.	2.690

It is that of a typical granite in all respects and needs no special comment. The water is of course from alteration. It may be remarked here that in this as in the following analyses the water was actually weighed as such during the process of the analytical investigation. This analysis was made from a specimen taken from an outcrop on a little hill in the N.W. corner of D 4, the freshest and best exposure found. From here as one goes southwest and south the granite becomes more and more dynamo-metamorphosed, and one of the most striking examples and best exposures of this is found in a recently worked outcrop just inside of Mr. J. Wharton's gate in the middle of C 3. Here the rock has been much fractured, it is full of slickensides and other evidences of shearing and pressure. Under the microscope all the components are seen to be broken and crushed; they lie in a mass of broken material which cemented together by secondary silica renders the rock extremely similar to a metamorphosed grit It is indeed similar to a grit only mechanically made. Epidote and other secondary minerals abound. In other places as along the shore of Mackerel Cove the rock exposures have suffered so much

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in addition from weathering that it would be difficult if not impossible to distinguish former granite from the conglomeratic grit occurring there if it were not for the large feldspar phenocrysts with *crystallographic outlines* which serve to differentiate it (additional to the included shales in the grit).

Aplite.—This presents the usual panidiomorphic mixture of orthoclase and quartz with a very little plagioclase, a little iron ore and the ferro-magnesian minerals almost wholly wanting. It has suffered greatly from pressure. Remains of micropegmatite structures can be detected at times.

*Micro-pegmatite* which occurs as mentioned in the central apophysis is very typical and comparatively fresh. It does not appear to have suffered so much from dynamic forces as the foregoing rocks.

Minette.-As before mentioned there are two dikes of this lamprophyre rock on the lower portion of the island as shown on map No. 1. The best and most unaltered exposure is found at Hull's Cove. The rock here is of a dark reddish rusty color on exposed surfaces, stained by iron oxide. On a fresh break it is of a dark gray, and fine grained, in which phenocrysts of biotite, at times several mm. in diameter, may be seen. Small fragments of the shales through which it has broken up may at times be found in it altered to a siliceous hornstone. Owing to the dynamic pressure the rock has received it breaks with a somewhat schistose fracture at times. The exposure of the second and southern dike at Lion's Head is similar only as the dike is smaller it has suffered more severely from squeezing and has a more pronounced schistose structure and the biotite phenocrysts are more rarely seen. The other exposure of this dike at the south point of Austin's Hollow shows these points in a still higher degree, the rock is completely schistose and is recognized only as a dike by its cutting across the strike of the shales, by its same reddish weathering color and by its strike being such that it must be the continuation of the Lion's Head outcrop. These points of identification are confirmed by the microscopical examination. The outcrop of the northern dike on Austin's Hollow was not visited by the writer but is given on the authority of Dr. Foerste. Under the microscope the freshest and best example of these rocks, from Hull's Cove is seen to be composed chiefly of orthoclase and biotite, the latter in two generations. Apatite, zircon, pyrite in well formed idiomorphic crystals and pretty abundant in amount; plagioclase and calcite are also largely present. Some secondary quartz occurs. The structure where it has not been destroyed is panidomorphic or allotriomorphic granular.

The rock is in that first stage of alteration of a lamprophyre which may be called the carbonate stage; it effervesces when placed in acids, but the second stage of alteration in which these rocks lose their carbonates and pass into masses of impure clay, and which may be termed the kaolin stage, was nowhere observed in either dike. The chemical composition is given

SiO,	46.11
SiO <sub>2</sub> TiO <sub>2</sub>	•84
X	·97
Al <sub>2</sub> O <sub>3</sub>	14.75
Fe <sup>2</sup> <sub>2</sub> O <sup>3</sup> <sub>3</sub>	2.20
FeO	4.51
MnO	tr.
MgO	5.73
CaO	7.82
Na <sub>o</sub> O	1.29
$\mathbf{K}_{2}\mathbf{O}$	3.84
$H_{2}^{2O}$	2.90
$\operatorname{CO}_{q}$	$\frac{2}{7}.32$
$S_{1}$	1.37
D	1.01
- Total	00.65
$\begin{array}{c} \text{Total} \\ \text{O} = \text{S} \end{array}$	<i>99</i> 00
0 = 5	.99
	0.0.00
	99.32
Sp. G	2.904

in the above analysis. The amount of  $CO_2$  shows the considerable amount of carbonates present and the sulphur that of the pyrite. The symbol X refers to the oxides of those earths which after fusion with HKSO<sub>4</sub> do not dissolve in cold water. It is probably more or less impure with zirconia, titanic oxide, etc. No attempt was made to determine it.\* A comparison of the chemical composition of this rock with that of minettes from other parts of the world shows a striking agreement with some of them as given in Roth's Tabellen.

The same rock in other portions of the dike exhibits the effects of pressure. The mica leaves are bent and curved, they begin to disappear and their place is taken by a cloudy decomposition product which shows perfectly the form and cleavage of the original biotite crystal. All grades of transitions may be traced from the unaltered crystals to those completely changed. On examining this cloudy alteration product with the highest powers it is found to be full of minute rutile needles and prisms. While other effects of pressure are clearly visible, this is one of the most noticeable in this dike

\* Conf. Williams' Igneous Rocks of Arkansas, Ark. Geol. Surv. Ann. Rep., 1889, vol. ii, p. 226, who gives full literature, etc.

AM. JOUR. SCI.—THIRD SERIES, VOL. XLVI, NO. 275.—Nov., 1893. 26 rock. The Lion's Head dike is precisely similar, only as it has been more highly pressed it shows this change in a higher degree and this reaches its highest development in the outcrop on S. point of Austin's Hollow. Here the rock is strongly folded in the strata and as already mentioned it has a pronounced schistosity. Also under the microscope it shows a schistose structure and contains considerable white mica and chlorite along with the broken material of the original rock, and were it not that all grades of transition from the nearly normal rock at Hull's Cove down to these forms can be traced, it would be impossible to recognize its original composition.

*Phyllite.*—It would be impossible to give here a minute description of all phases of the unaltered sedimentary rocks existing on the island. A pale greenish or gravish phyllite of extremely fissile character, however, is by far the most common rock, and it was selected for analysis. Thin sections of it from various places showed pretty nearly the same general character. Between crossed nicols with a moderate power the slice presents a dark gray "pepper and salt" appearance interspersed with fine points of brighter polarizing mineral frag-This is due to its excessively fine grain. Under very ments. high powers this is resolved into a mixture of sericite, chlorite. occasional fragments of feldspar (orthoclase and perhaps albite). specks of hematite, scales of graphite and pieces of quartz. Occasionally very minute but idiomorphic crystals of tourmaline The chlorite and mica, interwoven into a fine mesh occur. and strung out along the planes of schistosity, are with the quartz the chief components. This is everywhere penetrated

SiO,	56.36
$\operatorname{SiO}_2$ $\operatorname{TiO}_2$	0.97
Al <sub>2</sub> Õ <sub>3</sub>	22.78
Fe <sup>0</sup> O <sup>3</sup>	1.04
FeÖ	6.25
MnO	0.12
MgO	2.40
CaO	none
Na <sub>o</sub> O	1.48
K,Ó	3.91
H <sub>2</sub> O	5.01
-	
Total	100.35

by swarms and clouds of the most minute rutile crystals. Muscovite occurs at times in tabular crystals which in their orientation bear no reference to the planes of schistosity. The chemical composition of a specimen from Potter's Point is given in the above analysis. Lime was carefully tested for but not even a trace precipitated. It seems to be a very pure and typical phyllite. Even in the clearest and most uniform examples the original bedding shows in slight changes of a color banding across the cleavage planes.

Contact metamorphic rocks.—From what has already been said in the foregoing it is evident that no safe petrographical conclusions can be drawn concerning the nature of the metamorphism which has been effected in the sedimentaries by the intrusion of the granite. For the original strata varied rapidly in thickness and in character; their exact stratigraphical position in relation to the granite can no longer be made out, they have suffered from dynamic forces and from weathering as well, each bringing its own series of changes. The original character therefore is strongly masked and can only at times be suspected. Their geological relations are indeed far better seen and studied in the field than with the microscope though the latter reveals some interesting facts.

The first stage of alteration, where the shales assume a knotted appearance, has been sufficiently described, what follows relates to the harder and tougher hornstones. The dark solid slate-like rock occurring on the shore in a recent cutting in the lower part of E 6 shows an extremely fine grain consisting of quartz, white mica, specks of graphitic matter and iron ore with groups composed of masses of fine crystals that appear to be epidote and zoisite. These are strung along in a schistose structure. All through it appear places with less highly doubly refracting material that between crossed nicols show idiomorphic outlines and seem like pseudomorphs or phantom shapes of some former mineral that appeared in porphyritic crystals.

A very common form of the hornstone rocks is one composed chiefly of quartz and chlorite together with white mica, iron ore, etc., in allotriomorphic structure. This is assumed to be a rock which was formerly composed chiefly of quartz and biotite. It generally occurs pretty near the granite and composes largely the outcrops of E 4, lower E 5 and to the west of the road in D 5. It occurs also in direct contact with the granite in F 4 on Bull's Point.

Another form is that which occurs in the outcrop south of Mr. Green's barn in D 5 and east of the road. This as remarked before begins with a rock which has not entirely lost its shaly character. The rock consists essentially of quartz, white mica, fragments of feldspar, chlorite, bits of graphite and iron ore being freely sprinkled through it. Sections cut from the rock to the south of this show in addition a development of hornblende crystals in stringy forms mixed with masses of fine crystal particles of very low double refraction and high single refraction and which appear like masses of zoisite. Still farther southward this character of the rock together with the amount of hornblende increases. A somewhat similar form is found on Bull's Point and in addition some triclinic feldspar is present. It is indeed possible, as suggested by Dr. Foerste, that some former basic eruptive rock was present and included in the metamorphism produced by the granite, although in this case it could have formed but a relatively small proportion of the triangular altered area and its characters are now too much obscured for recognition. On the other hand the presence of feldspar as a result of contact metamorphism is well known especially in such rocks as contain a considerable amount of alkalies as suggested by Harker.\*

Mineralogical Petrographical Laboratory, Sheffield Scientific School, New Haven, June, 1893.

# ART. LII.—A Larval Form of Triarthrus; by C. E. BEECHER.

IN the August number of this Journal, Mr. W. D. Matthew made the important announcement of the discovery of antennæ and other appendages of *Triarthrus* found by Mr. W. S. Valiant near Rome, N. Y. The Yale Museum has received considerable material of a similar nature, which will doubtless furnish additional details of the structure of this trilobite. In the preliminary examination of this material, a number of larval specimens have been discovered, and several other points of interest observed, a few of which are here noticed.

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A description and illustration of the nearly complete metamorphoses of *Triarthrus Becki* was given by Walcott in 1879,<sup>†</sup> based upon specimens from near Holland Patent, N. Y. The earliest stage then known in this genus consisted of individuals having the cephalon and pygidium defined and one thoracic segment. With the new material, it is now possible to add an earlier stage in which the thorax is undeveloped and the cephalon predominates, while the other parts are not clearly differentiated. This stage corresponds to the earliest yet discovered in other genera; as in *Sao*, *Ptychoparia*, and *Acidaspis*.

The larval *Triarthrus* at this period is ovate in outline, widest behind, where it also attains its greatest convexity.

\* Quar. Jour. Geol. Soc., Aug., 1891, vol. xlvii. † Transactions of the Albany Institute, vol. x. The frontal margin is marked by a convex fold of the test. The axis is annulated. The anterior six annulations apparently belong to the cephalon, the sixth one being considerably stronger than the others and probably representing the occipital ring. The pygidial portion is defined by a narrow shallow transverse furrow; and the axis has two annulations.

Near the lateral anterior margins are two slight elevations which may represent the palpebral lobes of the eyes, and from them extend two furrows curving inward to the axis and dividing the cephalic region into two portions. The occipital pleura are indicated by slight depressions extending from the occipital ring.



The specimen illustrated in figure 1 has a Figure 1.-Trilength of .63mm and a width of .46mm.

arthrus Becki; dorsal view of larva.  $\times$  30.

Nearly all the specimens with appendages are complete, and lie with the ventral side upward. A few isolated fragments only have been observed. Individuals of all ages occur, the majority being about half grown.

So far as noticed, the other species of fossils, which are found strictly in the same association, are young individuals of Trinucleus concentricus, Schizocrania filosa, Leptobolus insignis, and Orthis (Dalmanella) testudinaria, ostracoda and graptolites of several kinds, indicating that the deposit belongs to the Utica slate.

Yale Museum, New Haven, Conn., Oct. 9th, 1893.

ART. LIII.—The Rise of the Mammalia in North America;\* by HENRY FAIRFIELD OSBORN, Columbia College, New York.

[Vice-Presidential address before the American Association for the Advancement of Science, Section of Zoölogy, Madison, Wisc., August 17th, 1893.]

TWENTY years ago an era opened in the mammalian paleontology of Europe and America. Partly inspired by the Odontographie of Rütimeyer, Kowalevsky completed and published in 1873 his four remarkable memoirs upon the hoofed mammals. He wrote these four hundred and fifty quarto pages in three languages not his own, in French upon Anchitherium and the ancestry of the horses, in English upon the

<sup>\*</sup> Some passages in this address have been omitted as indicated by dotted lines. The address will be printed in full in the Biological Studies of Columbia College, Part I.

## 380 H. F. Osborn-Mammalia in North America.

Hyopotamidae, in German upon Gelocus, Anthracotherium and Entelodon including the first attempt at an arrangement of a great group of mammals upon the basis of the descent theory. These memoirs swept aside all the dry traditional fossil lore of Europe; they breathed the new spirit of Darwin, to whom the chief one was dedicated, making principles of descent of more importance than new genera and species. Kowalevsky thus summed up the contemporary paleontology:

"After the splendid osteological investigations of Cuvier had revealed to science a glimpse of a new mammalian world of wonderful richness, his successors have been bent rather upon multiplying the diversity of this extinct creation, than on diligently studying the organization of the fossil forms that successively turned up under the zeal of amateurs and collectors. . . . With the exception of England (referring to Owen, Huxley, Falconer, and others), where the study of fossil mammalia was founded on a sound basis, and some glorious exceptions on the continent (referring to Rütimeyer, Gaudry, Fraas, Milne-Edwards), we have very few good paleontological memoirs in which the osteology of extinct mammals has been treated with sufficient detail and discrimination; and things have come to such a pass, that we know far better the osteology of South American, Australian, and Asiatic genera of fossil mammals than of those found in Europe."

At the same time, between 1869 and 1873, the pioneers of American paleontology, Leidy, Marsh, and Cope began the exploration of our ancient lake basins rich in life. The first ten years of their work not only revolutionized our ideas of mammalian descent, but brought together the data for the generalizations of the second decade; for Marsh's demonstration of the laws of brain evolution in relation to survival; for Cope's proof of ungulate derivation from types with the simple foot resting upon the sole, and with the conic or bunodont ancestral molar tooth; and finally for Cope's demonstration of the tritubercular molar as the central type in all the mammalia. These four generalizations furnished a new working basis for morphology and phylogeny.

In these twenty years, thanks to energetic field work, we have accumulated vast materials for the history of the rise of the mammalia, enough for ten students where there is one, and the question arises : how shall we take best advantage of it, what methods shall we adopt? In this address, besides bringing before you the more recent achievements of exploration and research, I will try to illustrate the advances already made in lines of thought, observation and system in paleontology and indicate other advances which seem to me still desirable. In the problem of how to think and work most effectively, and with most permanent results, all the sciences meet on common ground.

#### Advances in Method.

It is to the renown of the veteran Rütimeyer and of Kowalevsky, so soon unfortunately deceased, that, while their main inductions suffer by American discoveries, their methods of thought have not been displaced. It matters little that their theory, that ungulate molars sprang from lophodont or crested forms, has been disproved; that Kowalevsky's tables of descent are full of errors; that his main generalization as to the persistence of adaptive and extinction of inadaptive foot types does not hold good; that the horses and Anchitherium spring not from Paleotherium as he supposed, but from Pachynolophus and Hyracotherium, types which he carefully studied and yet omitted from the horse line! It is the right system of thought which is most essential to progress; better in the end wrong results such as the above, reached by the right method, than right results reached hap-hazard by a vicious method. If a student asks me how to study paleontology, I can do no better than direct him to the Versuch einer natürlichen Classification der fossilen Hufthiere, out of date in its facts, thoroughly modern in its approach to ancient nature. This work is a model union of the detailed study of form and function with theory and the working hypothesis. It regards the fossil not as a petrified skeleton, but as moving and feeding; every joint and facet has a meaning, each cusp a certain significance. Rising to the philosophy of the matter, it brings the mechanical perfection and adaptiveness of different types into relation with environment, the change of herbage, the introduction of In this competition it speculates upon the causes of grasses. the rise, spread and extinction of each animal group. In other words the fossil quadrupeds are treated biologically-so far as possible in the obscurity of the past. From such models and from our own experience we learn to feel free to abandon traditions in the use of the tools of science, such as mere methods of description and classification, and to regard priority in nomenclature only.

New discoveries continually produce new conditions: there is nothing more obstructive than the reverence for old ideas and systems which have outlived their usefulness. In observation, an old principle was *de minimis non curat lex*; now, we cannot be too exact. Every cusp and facet has its value, not as a sign-post for a new species, but as suggestive of some function or relationship. Bird's eye methods of comparison, which, for example, find no difference between a rhinoceros and a lophiodon molar, are of no service now that we are

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called upon to distinguish between so many lines of ancient mammals crowding in among the ancestors of existing mammals. Again, paleontology is not a science apart; it has always gone hand in hand with recent osteology; it must now keep abreast with the embryology of the teeth and skeleton; with the animal mechanics of Marey, Allen, and Muybridge; with paleobotany, geology, and historical physical geography. In these points we cannot be too broad. All structures should be considered as to their homologies, their mechanics, which throw such a brilliant light upon their evolution; their relations to the food and soil, and to other parts. This brings us to the animal as a whole—its tendencies, its place in the system of descent, its relations to its contemporaries, the causes of its progression or retrogression; finally, into pure speculation. Here I am reminded of a critical saying by the late Professor v. Gudden, the distinguished neurologist: "Ein Steinchen der Wahrheit hat mehr Werth als ein grosser Schwindelbau;" it was in allusion to the temporary character of the great nerve-tract systems of Meynert and Flechsig. The great 'Schwindelbau,' literally the 'disappearing structure' of paleontology, is the phyletic tree which adorns the end of many good as well as superficial papers; and recently, because of its extremely brief life, has fallen somewhat into disfavor. I do not think the present reaction against these 'trees' is a wise one; we must remember they are the working hypotheses of our branch of science and serve to most clearly express present knowledge.

To illustrate some of these principles of modern methods, let us first look at the evolution of the teeth in the rise of the mammalia. The teeth and the feet are the foci of mammalian evolution, the only direct points of contact with food and the earth. Their combined use in phylogeny has increased in interest, because their evolution has proved to be wholly independent. We recall Cuvier's famous law which Balzac said at the time: "Rebuilt like Cadmus cities, from a tooth."

No generalization has been more thoroughly routed than that of a necessary law of correlation between tooth and foot structure. Besides the orthodox clawed carnivores and hoofed pachyderms of the great French anatomist, we have discovered hoofed carnivores such as Mesonyx, and clawed pachyderms such as Chalicotherium. Even the apparently lasting barriers of correlation, which Owen raised between the even and oddtoed ungulates, have broken down by Ameghino's discovery of a Litoptern odd-toed horse with an even-toed type of astragalus. Not only is there no correlation of type, but none in the rate of evolution. Hipparion, the most progressive horse in tooth-structure, probably owed its extinction to its conservative preservation of its ancestral three toes. For these reasons the teeth and feet, owing to the frequent parallels of adaptation, may wholly mislead us if taken alone; while, if considered together, they give us a sure key; for no case of exact parallelism in both teeth and feet between two unrelated types has yet been found, or is likely to be. This, I believe, is the one lesson of later work which reverts to older methods; we should not base either classification or descent upon the teeth or feet alone. Every additional character diminishes the chances of error.

The evolution of foot structure has now become a science and advances have been made in the principles of progression from the plantigrade, pentadactyl serial types to the unguligrade, monodactyl alternating types which are of the greatest importance in classification and phylogeny. It is surprising how little attention was given to ungulate foot structure between the time of Cuvier and Kowalevsky. Owen's generalization as to the Artiodactyl and Perissodactyl pes formed the one bright exception. Kowalevsky first directed attention to the importance of the more median metacarpals displacing or spreading to gain a stronger foothold upon the carpals as the lateral toes disappeared. Ryder also worked out the laws of reduction. The discovery of Phenacodus led Cope to the final generalization that the primitive ungulates were not only plantigrade but had some of their carpals and tarsals in vertical rows like bricks clumsily set with unstruck joints-and that one great law of evolution towards digitigradism was to produce diplarthry or alternating joints. As he found this alternation differed both in degree and kind in different groups, he revived the comprehensive "Ungulata," of Linnæus and divided all hoofed mammals exclusively upon their foot structure into five great orders.

Rütimeyer and myself have shown that however successful and convenient this system appears, Cope's lines of division ignore the fundamentally different modes of evolution of the fore and hind feet; an animal may be a taxeopod in front and a diplarth behind or *vice versa*. Numerous exceptions to Cope's definitions are also found. The discovery of the aberrant ungulate foot types of South America further invalidates Cope's system and sustains the principle that to be permanent classification must be based upon at least two entirely diverse sets of characters. This does not diminish the importance of the primitive taxeopod plantigrade type as one great key to the still unsolved problems of the primary relationships of the Condylarthra, Hyracoidea, Amblypoda, Proboscidia, Toxodontia, Litopterna, Artiodactyla and Perissodactyla. All these orders still stand apart in the dim past like so many mile-posts. While Cope overestimates the feet in these larger divisions, many writers in Europe still depend wholly upon the teeth and ignore the wide degrees of divergence such as are indicated in the Perissodactyla for example in functional tetra-, tri- and mono-dactylism. By "functional" we refer to *tendencies* which are not expressed in the bare digital formulas—and which have the same relation to the feet that the dental curve has to the teeth. The evolution of a monodactyl tendency is not the work of a century but of a geological period, a principle which we wholly ignore when we place the monodactyl Anchitheres with the tridactyl Palæotheres, on the ground that their dental type and digital formulæ are identical. How many toes an animal has is of far less importance than how these toes are being displaced and reduced.

#### Lower Mesozoic Pro-Mammalia.

With the exception of the triassic *Theriodesmus* of Seelye, no mammal is known by its limbs or skeleton until we reach the basal Eocene; in studying the first steps in the rise of the mammalia, we are thus practically driven to the teeth and jaws alone. In these straits of the fossil-hunter, embryology has lately come famously to aid.

Assuming their remote reptilian origin, agreeing with Baur and Kükenthal that the theromorph reptiles were parallel with rather than ancestral to the mammals, and therefore placing before both groups the hypothetical *Sauro-mammals* in or below the Permian, we come to the old question which Huxley discussed in his famous anniversary address: "Was there a succession between Monotremes, Marsupials, and Placentals, or a parallel development from a common pro-mammalian type?" Then we look to the newer questions, "When were the Edentates and Cetaceans given off?"

Modern tooth-science springs first from the recent demonstration of Rütimeyer's hypothesis of 1869, that the teeth of all the mammals center around a single reptile-derived type. With a single exception, which I believe can be disposed of, various stages of trituberculism or a three-cusped condition have become the standard for the teeth, as pentadactyly has long been for the feet, except that this is developed within the mammalian stem, while our five fingers are a reptilian legacy. Second, it springs from the recent thorough exploration of the youngest jaws for evidences as to the primitive form and succession of the teeth. This also supports the reptile theory of tooth descent by proving, what has been in considerable doubt, that the Pro-mammalia had a multiple succession of teeth like the reptiles, and that even some of the modern mammals retain dim traces of four series of teeth.

The brilliant discoveries of Kükenthal, Leche, and Röse begin to show how in various ways the mammals early modified the regular succession of all the teeth by suppression of parts of the multiple series ; this is the first thing to consider. The next is how heterodontism arose, how the conic rows of teeth were specialized in different parts of the jaw for three or four functions; as a certain number of teeth took up each function, the question arises whether this number or dental formula was ever the same in all the mammals, for we know it is very different now. After the teeth were thus divided, some functions became more important than others, and established a monopoly, causing first a marked difference in the relative development of the series, which we may express in a dental curve, resulting finally in a loss of certain teeth. In the meantime began the special evolution of the form of the back teeth, or molars. Was this alike in all mammals, was it tritubercular? It is surprising how many problems of early relationship are at stake in these simple processes.

# Primitive Diphyodontism.

What does *succession* really consist in? It now appears that Baume was right in denying that the first tooth is the mother of the second; for the teeth of the lower as well as the upper series, spring from the common epithelial dental fold (Schmelzleiste) which dips down from the surface and extends the whole length of the jaw; at intervals it buds off the dental caps (Schmelzkeim) of the first series: after these are separated off, the dental fold sinks and buds off the dental caps of the second series, always below and inside the first ; thus the fold is the mother and the caps are sisters, twins, or triplets, according to the number of the series. In all young mammals, including the traditional monophyodont Cetaceans and Edentates, and excepting only the still unexplored Monotreme embryos, traces of two series of teeth have been found. Both Leche and Röse have detected evidence that the dental fold sometimes buds off parts of a third series, thus explaining the occasional reversion of supernumerary teeth on the inner side of the second series, and Leche has seen traces of budding preceding the first series-thus giving us vestiges of four successions !

All our perplexities as to the relations of the milk and permanent teeth, and the ingenious but mistaken hypotheses of Baume, Flower, Wortman, have sprung from our want of evidence of the regular and complete diphyodontism of the stem mammals. The solution in brief is that the "milk teeth" and the "true molars" are descended from the first series, while the second series is represented by the "permanent incisors canines, and premolars" and rudiments of dental caps beneath the true molars. The mammals early began to diverge from this primitive diphyodontism in many ways; apparently adapting the first and second series, respectively, to their infant ard mature feeding habits; losing parts or all of one series or the other, and in some cases pushing teeth of the second series in among the first; this intercalation has been a most confusing factor to us.

In the Marsupials (Kükenthal) almost the entire first series became permanent; thus from the Jurassic period to the present time only a solitary fourth premolar of the second series has pushed out its elder sister tooth, and Röse has observed that an outer upper-incisor also pushes up from the second series; the remainder of the second series still persist as rudimental dental caps beneath the first, even beneath the first and second molars! There are wide variations among the Placentals; thus in the lowest existing forms, the Insectivora, Leche finds that in the Shrew (Sorex) the second series is suppressed entirely, while in the Hedgehog (Erinaceus) of the twelve permanent teeth in the anterior part of the jaws five belong to the first series and seven to the second. We thus meet with the paradox, that among the "primitive" Marsupials and Insectivores the regular reptilian succession was early interrupted, while in all the "higher" mammals the reptilian succession of two series was retained in the anterior part of the jaw. Beneath the posterior highly specialized molar teeth of both Marsupials and Placentals, the second teeth were early suppressed, although in the Edentates, which also originally had specialized molars, there is a typical succession of seven teeth behind the canine. These discoveries prove that the whale teeth, like their paddles, have acquired a secondary adaptive resemblance to those of the Icthyosaurs. How did the single and simple teeth of the Edentates and Cetaceans develop? Clearly by retrogression. As Leche points out in the aquatic Carnivora, in which the first series are degenerating, the single-series condition (monophyodontism) advances step by step with retrogressive simplification of the tooth form (homodontism); thus in the true seals, the eared seals and the walruses, as the permanent teeth become simpler, the milk teeth become smaller. The Edentates, so widely separated genetically, parallel the seals in tending to suppress the first series of teeth and simplify the crowns of the second series at the same time. We might jump to the conclusion that this gives us an explanation of the homodont and apparently monophyodont condition of the toothed whales, especially as it has been supposed they sprang from aquatic Carnivora, but in this

order matters were reversed, for the first series persisted and the second series were suppressed and persist as a rudimental row of tooth caps buried in the jaw.

Each dental series has an adaptive evolution of its own, in Erinaceus the first series has an ancient and the second a modern form; in Ericulus both series are alike; in the Bats the first series is homodont the second is heterodont (Leche); in the Edentates the first series is ancient and heterodont the second is modern and homodont (Thomas, Rheinhardt); so among the Cetacea and Ungulata.

What deep and ancient clefts the different laws of succession mark between the Marsupials and these three Placental groups.

### Primitive Heterodontism and Formula.

Now that all mammals are led back to a distant diphyodont stem, it is also true that the further we go back both in palingenesis and embryogenesis, the more widespread heterodontism is—all modern homodontism proving to be secondary. The simple conic teeth of the porpoise, for example, bear a misleading resemblance to those of a reptile. Flower, Weber, Julin, and Kükenthal agree that the ancestral whales and edentates were heterodont and had a smaller number of teeth than the existing forms.

Heterodontism is then the second problem. When did the division of the teeth into incisors, premolars, and molars occur, before or after the Monotremes, Marsupials, and Placentals separated? It is well settled that the canine was the first maxillary tooth, and developed from the most anterior bifanged premolar; also, from the discovery of complete succession, we must now define the first molar as the most anterior specialized or triconid tooth, not as the most anterior permanent tooth. It seems to me we now find strong evidence that the stem mammals had a uniform number of each kind of teeth; in other words, a uniform dental formula. Monotremes are most in doubt as the existing forms point only to primitive heterodontism. It will be a great step forward when we learn whether or not the Multituberculates are Monotremes-the resemblance of their molars to those of the Duckbill is very superficial, for the Duckbill upper molars lack the intermediate row of tubercles universally seen in the Multituberculates, and look to me rather like degenerate Trituberculate teeth. Cope has recently found in the Cretaceous rocks a remarkable Trituberculate, which he names Thlaeodon ; the jaw of this animal is neither Placental nor Marsupial; it is like that of the Multituberculates-and both resemble re-

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motely the degenerate modern Monotreme jaw. All we can say, therefore, is that the Multituberculates are an archaic group, highly specialized even in the Trias, that they were *probably* Monotremes, and neither structurally nor functionally akin to the Diprotodont Marsupials (Owen) nor to the Microbiotheridæ (Ameghino). With a dental mechanism and a condyle exactly like that of the rodents, they show no trace of canines, and the mode of evolution of their peculiar molars was probably paralleled later in the rodents. They present vestiges of a primitive dental formula, like this: I 3C? P 4. M4+. Thlaeodon shows C1, P4, M3. Thus, so far as this doubtful paleontological evidence goes, the Monotremes had a typical formula.

Our next step is to unify the typical 5, 1, 3, 4 of recent Marsupials with the 3, 1, 4, 3 of higher Placentals. Thomas has shown in his studies of recent Marsupials that they have probably lost one of the four typical premolars (pm. 2); this observation, fortunately, is partly confirmed by Röse's finding an embryonic germ of this tooth. Ignoring the incisors of the Jurassic Marsupials, Thomas raised the number of ancestral incisors to five, the highest number known among recent Marsupials; Röse therefore made another step towards uniformity when he showed that the Marsupial i.5 is probably a member of the second series of incisors, and should not be reckoned with the first. Now, if we suppose that the Placentals have lost one incisor, and one molar (abundant evidence of which is found in Otocyon, Centetes and Homo), we derive as the ancestral formula of both orders :

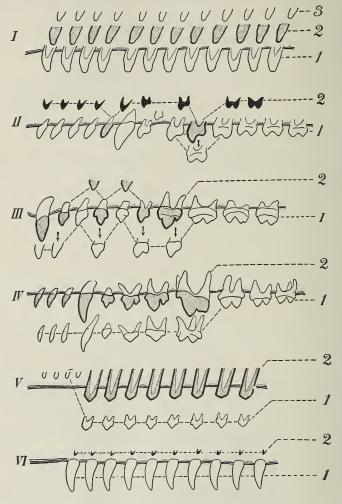
Incisors, 4; Canines and Premolars, 5; Molars, 4.

The aberrant placental Cetacea point in the same direction as we read in the conclusion of Weber's fine memoir: "All the Cetacea sprang from a stem with a heterodont, but only partly specialized dentition (something like that of Zeuglodon, 3, 1, p & m: 7), . . . not direct from Carnivores or Ungulates, but from a generalized mammalian type of the Mesozoic period, with some affinities with the Carnivora. . . . Zeuglodon itself branched off extremely early from the primitive line, and the heterodont Squalodon (mark its formula, 3, 1, 4, 7), "branched off later from the toothed whale line, after the teeth had begun to increase in number and before homodontism had set in." It would be easier for us while speculating to take Squalodon and the Odontocetes directly from the Jurassic mammalian formula (3, 1, 4, 8). As for the multiplication of this formula, we have found the way, says Kükenthal, by which numerous homodont teeth have arisen from a few heterodont molars, it is by the splitting up of the numerous triconid molars of Jurassic ancestors into three. He substitutes this hypothesis

for the one advocated by Baume, Julin, Weber, and Winge, that the multiple cetacean teeth represent the intercalation or joint appearance of both the first and second series of teeth, owing to the elongation of the jaw—a view which is now disproved by Kükenthal's discovery of the second row beneath the first. Since even by Kükenthal's hypothesis the typical Mesozoic mammals could not furnish as many teeth as are found in some of the dolphins, a likelier explanation than his seems to be that as the jaws were elongated the dental fold was carried back and the dental caps were multiplied.

The Edentates, like the Cetaceans, point back to heterodontism, and somewhat less clearly to a typical dental formula. We are here indebted to Flower, Rheinhardt, Thomas, Kükenthal, and Röse. It is their rudimental and useless first series which gives the evidence of heterodontism, while the second series has become adaptively rootless and homodont. The especially aberrant feature is that a double succession exists in the typical "true molar" region. The adult nine-banded Armadillo presents only eight maxillary teeth, seven of which are preceded by two-rooted milk teeth (Tomes); in the embryo Leche finds fifteen dental caps, of which only thirteen are calcified; this number probably includes the four rudimentary incisors observed by Rheinhardt. In the aberrant Oycteropus (Aard-Vark), with ten adult teeth, Thomas finds seven milk teeth behind the maxillary suture (thus taking us into the molar region of the typical heterodonts). The last of these milk teeth is large, and two-rooted ; behind this are three large permanent posterior teeth, apparently belonging to the first series. The large lateral tooth of Bradypus is suggestive of a canine. From this rapidly accumulating evidence it appears probable that the ancestral Edentates had four incisors, a canine and eight or more teeth behind it, the double succession extending well back so that the first series did not become permanent at the fifth tooth behind the canine as in the Marsupials and higher Placentals. If these are primitive conditions, as seems probable from comparison with fossil Edentates, they carry the divergence of the Edentates, like that of the Cetaceans, back into the Mesozoic period. Comparative anatomy and embryology thus point back to highly varied branches of a generalized placental heterodont stem in the Mesozoic, and a much earlier divergence than we formerly imagined. Now let us see what the early Mesozoic mammals point forward to.

There are three distinct and contemporary Jurassic types, the Multituberculates, the Triconodonts, and the Trituberculates. Are not these the representatives of the Prototheria, Metatheria, and Eutheria? In the archaic Multituberculates we have seen a monotreme type of jaw and vestiges of a typical ancestral formula. The Triconodonts are a newer group, perhaps derived from the Dromotheriidae (incipient Triconodonts) of the Trias although these appear to be aberrant; the typical forms extend from Amphilestes to Triconodont,



and exhibit the first stages of development of the inflected Marsupial jaw. The Trituberculates include the Amphitheriidae and Amblotheriidae with true tuberculo-sectorial lower molars, like those of modern Insectivores; they alone exhibit the typical angular placental jaw,—no reason can be assigned for calling them Marsupials, excepting the traditional reverence for the Marsupial stem theory. Now, it is very significant that the average dentition of these old but highly diverse forms, namely, Multituberculates, 3?, 4, 6, Tricono-donts, 4, 1, 4, 7, Trituberculates, 4, 1, 4-5, 8, is also the dentition to which the existing mammals apparently revert.

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Thus, the tendency of late research is to show that all stem mammals were related in their double succession, in their dental formula, and in their primitive molar form. These features point, not to a succession, but to a unity of ancestry of the Monotremes, Marsupials, and Placentals.

### Divergence of the three Groups.

The discovery of the complete double series seems to have removed the last straw from the theory of the Marsupial ancestry of the placentals, for the peculiar mode of suppression of the second series in the Marsupials has been constant since the Purbeck; this difficulty is added to the structure of the jaw, the epipubic bones, the profoundly different mode of foetal nutrition. None the less, any conclusion we can draw now as to the primary relations of the three great groups is more or less of a "Schwindelbau," and I put together the results of these later discoveries with a full realization of the temporary character of present conclusions.

The Permian Sauro-Mammalia (Baur) with a multiple succession of simple conical teeth divided into : A, Theromorpha, which lost the succession and in some lines acquired a heterodont dentition and triconid single-fanged molars; B, Promammalia.

The hypothetical lower Triassic Promammalia retained a double succession of the teeth; they became heterodont, with incipient triconid double fanged molars; dental formula approximating 4, 1, 4-5, 8. They gave rise to three groups: I. The Prototheria which passed rapidly through the tritubercular into the multitubercular molars in the line of Multituberculates, and more slowly into trituberculy and its later stages in the line of Monotremes. II. The Metatheria or Marsupials tended to suppress the second series of teeth, except those intercalated with the first; by this and by reduction the formula became 5, 1, 3, 4-6; the molars passed slowly through the triconodont into the typical tritubercular type. III. The Eutheria or Placentals divided early into a number of branches, in which there was heterodontism, but no uniform modification of succession, namely: A, forms suppressing the second series in the molar region only, and acquiring a typical Eutherian dentition, 3, 1, 4, 3-4. 1. The Insectivores tended to partly

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suppress the anterior teeth of the second series or intercalate them with teeth of the first series; the molars became trituber-2. The higher Placentals retained the succession of cular. the first and second series as far back as the first molar; the molars entered rapidly into trituberculy and its higher stages. B, forms retaining the double succession in part of the molar region, and retaining more of the primitive dentition, 4, 1, 4, 3. The Edentates branched off from an early triconodont 8. or tritubercular diphyodont stage, with numerous molars, and secondarily suppressed the first heterodont series, and established a numerous homodont second series. 4. The Cetacea also branched off from a diphyodont, heterodont stage, and secondarily established a numerous homodont first series, and suppressed the second series.

[To be continued.]

## SCIENTIFIC INTELLIGENCE.

### I. CHEMISTRY AND PHYSICS.

1. On the Effect of Temperature on the Rotatory Power of Liquids.—It has been shown by AIGNAN that in cases where a liquid is optically inactive because it is a mixture of two active substances of opposite rotatory powers, the inactivity, as a rule, will hold only for rays of a certain wave-length. In consequence the mixture will be active in one direction for rays of shorter wave-length and active in the opposite direction for rays of greater wave-length. This phenomenon is well shown, for example, with mixtures of lævogyrate terebenthene and dextrogyrate camphene. Moreover, in such liquids the optical equilibrium will be disturbed by a change of temperature; the liquid becoming active in one direction when the temperature rises and in the other direction when the temperature falls. This phenomenon, also, is observed with mixtures of terebenthene and camphene. With red rays the rotatory power changes sign between 61° and 73°, and with yellow rays between 13° and 33°; while with green rays the liquid is always dextrogyrate between 13° and 90°, the rotatory power increasing with the temperature. Phenomena of this kind were long ago observed by Biot in the case of solutions of tartaric acid. And the author suggests that the results obtained by Colson (C. R., cxvi, 319) are explicable on the supposition that the liquids used by him are mixtures of two substances of opposite optical activities, the variations in the rotatory power being due to the causes above mentioned. - C. R., cxvi, 725; J. Chem. Soc., lxiv, II, 354, August, 1893. G. F. B.

2. On the Flume Spectra of Metals.—The ultra-violet portion of the flame spectra of the salts of certain metals has been photo-

graphed by Cochin. For this purpose he used a spectrograph with quartz prisms and quartz and Iceland spar lenses, the gelatino-bromide film being curved so that all the lines were in focus. The water bands at wave-length 309 were obtained in all cases, but there were no lines or bands of higher refrangibility than this observed in any case, even when the exposure was quite long. In the case of the hydrogen flame the results are practically the same, though the spectra are somewhat more luminous. In these spectra, the line  $\lambda$ 413 of lithium is shown, and the double line  $\lambda$ 330.3 and  $\lambda$ 330.2 of sodium, obtained in the electric arc spectrum by Kayser and Runge. Rubidium, in addition to the visible line  $\lambda 420$ , gives the two doublets at  $\lambda 359.1-358.7$  and  $\lambda$ 335·1-334·8, observed by Kayser and Runge; especially if the hydrogen flame is employed. Cæsium gives the lines  $\lambda$ 388,  $\lambda$ 361.5 and  $\lambda$ 347.75, in addition to the visible blue lines  $\lambda$ 459.7-450; also corresponding apparently to lines seen by Kayser and Runge. No ultra-violet lines were observed in the spectra of calcium, strontium or barium, though the visible lines were photographed. Thallium gave lines at  $\lambda$ 353 and  $\lambda$ 378 in the ultraviolet; thus resembling the alkali-metals.-C. R., cxvi, 1055; J. Chem. Soc., lxiv, II, 402, September, 1893. G. F. B.

3. On the Spectrum given by Nickel-carbonyl.-According to LIVEING and DEWAR, nickel-carbonyl, when mixed with hydrogen and burned in oxygen at a porcelain jet, exhibits a spectrum which consists of two parts: (1) the spectrum of the main body of the green flame; and (2) that of the base of the flame. The spectrum of the main body consists of a series of shaded bands, brightest in the green but extending on the red side beyond the red lithium line and on the violet side well into the blue. These bands have their sharp edges on the more refrangible side. Besides the bands a few visible lines appear, only one of which  $\lambda 5476$  is a known line of nickel. In the ultra-violet part, however, a great number of nickel lines were photographed. In the spectrum of the base of the flame there are two principal groups of lines, one in the orange and red, the other in the citron and yellow. None of them appear to be nickel lines.-Proc. Roy. Soc., lii, 117; J. Chem. Soc., lxiv, II, 404, Sept. 1893. G. F. B.

4. On the Optical Properties of Liquid Oxygen.—By means of a specially constructed apparatus OLSZEWSKI and WITKOWSKI have succeeded in determining the angle of total reflection in liquid oxygen; and from this they have deduced the index of refraction of this substance. As thus found, the relative refractive index of liquid oxygen appears to be 1.2232 and the absolute index 1.2235; this latter value agreeing closely with 1.2236, that found by Liveing and Dewar. The absorptive power of a column of liquid oxygen one millimeter in thickness, between  $\lambda 577$  and  $\lambda 570$ , i. e., in the most intense portion of the yellowish-green absorption band, was found to be between 84 and 89 per cent; while for the red absorption obtained was 88 per cent.—*Chem. Centr.*, i, 595; J. Chem. Soc., lxiv, II, 353, August, 1893. G. F. B.

5. On the formation of Ozone from Oxygen.-An extended series of experiments has been made by SHENSTONE and PRIEST on the production of ozone by the action of the electric discharge upon oxygen, attention being paid especially to the effect of greater or less differences of potential, of the rapidity of the discharges and of the construction of the ozone generator. In producing ozone in this way the chief points requiring attention are the following: (1) the ozone generator should be cooled, which is best done with an apparatus of the Brodie form; (2) it should be made of the thinnest glass that can be drawn of the requisite size and uniformity; (3) its inner tube should fit fairly closely into the outer tube; (4) if a product rich in ozone be required, the oxygen should be passed through the ozonizer very slowly, the potential difference should not be too high and the breaks in the primary current should not exceed 1000 per minute; (5) if however the oxygen is to be charged with ozone rapidly, a higher potential difference may be employed, but the yield is less; (6) the best results are given by a large induction coil if the rapidity of its action be well managed. These experiments, the authors think, throw some light on the nature of the process itself, by which oxygen is converted into ozone. They show that unless the path of the discharge be very short, the proportion of oxygen converted into ozone, under given conditions as to temperature and pressure, is for a given ozone generator practically independent of the potential difference employed, provided that the range is of moderate extent. In other words they show that the ultimate effect of the discharge is conditioned only by the temperature and pressure at which the ozonizing is effected. Moreover, these experiments show that any circumstance which is likely to be opposed to the effective cooling of the gas (such as great frequency of discharge, or the employment of very high potential difference with a short path for the discharge) causes a falling off in the proportion of ozone formed; whilst any circumstance which promotes the efficiency of the refrigerating power of the ozone generator (such as employing the discharges at a low rate of frequency, or using an ozone generator the tubes of which fit closely, together with low potential difference) raises the proportion of ozone considerably. The authors regard these facts as supporting distinctly the view that the direct effect of the discharge is not to produce ozone but to resolve a greater or less proportion of oxygen molecules into atoms, and that the ozone is produced after the discharge by the recombination of these atoms; since if the formation of ozone depends on the recombination of the atoms of oxygen after the discharge, we should expect the proportion of ozone formed to be largely influenced first by the refrigerating efficiency of the generator and secondly by the temperature employed.-J. Chem. Soc., lxiii, 938, July, 1893. G. F. B.

6. On Nitrocopper.—The compound called by SABATIER and SENDERENS nitrocopper, is obtained by passing nitrogen tetroxide (peroxide) over finely divided metallic copper at 25-30°, this

copper being obtained by reducing copper oxide by means of hydrogen or carbon monoxide. It has the composition Cu, NO, whether made with pure tetroxide or with tetroxide containing nitrogen. Nitrocopper is permanent in dry air, but decomposes into copper and nitrogen tetroxide above 90°. It is violently decomposed by water, with the evolution of pure nitrogen dioxide and the formation of a solution of copper nitrite and nitrate. Hydrogen has no action in the cold but ammonium nitrate and free ammonia are formed when the temperature is rapidly raised to about 180°. Carbon monoxide likewise has no action in the cold but on heating nitrogen tetroxide is evolved and reduced copper is left. Sulphur dioxide on heating unites with the nitrogen tetroxide evolved forming the well known crystalline compound, and leaving a residue of partly oxidized copper containing some copper sulphate. Gaseous ammonia attacks it in the cold, forming water vapor and white fumes of ammonium nitrite and nitrate, the mass becoming suddenly incandescent, forming a large quantity of ammonium salts and leaving a residue of copper and ammonio-copper oxides. In short nitrocopper behaves as if while the copper and the nitrogen tetroxide were intimately associated together, each retained its own properties. - C. R., cxvi, 756; J. Chem. Soc., lxiv, II, 374, August, 1893. G. F. B.

7. A Dictionary of Applied Chemistry; by T. E. THORPE, assisted by eminent contributors. Vol. III., 1058 pp., 8vo. London, 1893 (Longmans, Green & Co.) .- This substantial volume of upwards of 1000 pages marks the completion of a work of no small magnitude, the successful accomplishment of which is a matter for congratulation, not only for the editor-in-chief and his associates but also for the chemical public as well. The general scope of the work and its relations to the original edition of Watts' Dictionary of Chemistry were explained in a notice in this Journal (vol. xxxix, 519, also xxxviii, 409) of volumes I and II. The third volume now issued contains more than two-thirds the amount of matter in the other volumes taken together. It is hardly necessary to state that the same high standard of excellence is maintained in the many interesting and well digested articles. Some of the subjects treated in greatest detail are the following : Petroleum, by Boverton Redwood; photography, by J. M. Thomson; soap, sulphur, sulphuric acid, by C. R. Alder Wright; spectrum analysis by W. N. Hartley; starch, by John Heron; water, by P. F. Frankland; the articles upon the metals and metallic salts are also to be noted. The value of the articles is increased by liberal illustrations and by the references to the general literature often given at the end.

8. Connection between ether and matter.—Since Fresnel's time the question has been debated whether (1) the earth carries with it the ether in its immediate neighborhood, thus causing a disturbance, or (2) rushes through it, and it through the earth, each being independent and moving independently. Dr. Lodge has endeavored to discover whether a rapidly revolving steel disc (like a circular saw) exercises any drag upon the ether in its immediate neighborhood. He uses two such discs of tough steel, above a yard in diameter, rotating in parallel planes an inch apart. Running the discs at 3000 revolutions per minute he can discover no effect which can be attributed to any drag of the ether. He has also replaced the discs by an oblate spheroid of wrought iron with a deep channel or groove cut in it and wound with wire; but the rotation of this transversely magnetized mass (weighing about a ton) does not set the ether in motion.—Nature, Sept. 28, 1893. J. T.

9. Chrono-photographic study of locomotion.—M. MAREY continues his work upon this subject. Reptiles are placed in a circular canal where they can run on indefinitely, the chrono-photographic apparatus being placed above the canal. Fishes are made to swim in a similar canal which is illuminated from above, so that they appear dark on a light ground. An eel and an adder progress in the water in the same manner. A wave of lateral inflexion runs incessantly from the head to the tail, and the speed of background propagation of this wave is only slightly superior to the velocity of translation of the animal itself. In fishes, provided with fins, and in reptiles possessing feet, there remains in general a more or less pronounced trace of the undulatory motion of reptation.— Comptes Rendus, Aug. 28; Nature, Sept. 7, 1893. J. T.

10. Electrical oscillations of very small wave-lengths.—RIGHI continues the description of experiments he has conducted on this subject (Nature, June 22, 1893). The oscillator consists of two small metal spheres surrounded with oil and held by two rods of ebonite. These spheres are placed between the discharging rods of a large Holtz machine. With spheres 4<sup>cm</sup> in diameter the wave-length of the radiation obtained was 20<sup>cm</sup>, while with spheres of 1.3<sup>cm</sup> diameter the wave-length was about 7<sup>cm</sup>. The resonator was of a novel form and was made from a rectangular piece of silvered glass of such a size that its breadth was equal to the length of the resonator required. The varnish was then dissolved off the back of the silver and a line drawn through the silver by means of a diamond, so as to divide the strip of silver into two equal parts, and form a spark gap. By this means a spark gap of one and two thousandths of a millimeter was obtained. For radiations of 7.5cm wave-length, the resonator was made of a strip of silver 3.9<sup>cm</sup> long and 0.2<sup>cm</sup> in breadth. With these small wave-lengths the sparks ceased to be visible when the distance between the oscillator and the resonator was a meter, but were visible at a distance of six meters from the oscillator when a parabolic metallic reflector was placed behind the resonator. The author has succeeded in producing interference by Fresnel's method of inclined mirrors. It was found that ebonite, paraffin and rock salt are perfectly transparent. A plate of mica 1.7mm thick absorbs 10 per cent of the electric radiation, while a plate of ordinary glass 8mm thick absorbs 37 per cent and a piece of

quartz cut normally to the axis S<sup>mm</sup> thick absorbs 40 per cent.— Trans. Acad. de Lincei; Nature, July 27, 1893. J. T.

11. Theory of electrical waves in wires.—A. ELSAS in a mathematical paper shows that the phenomena observed by Hertz can be explained on the old theories of the movement of electricity, developed by Kirchhoff, "Ueber die Bewegung der Electricität in Drähten" and also by Helmholtz. Maxwell's theory of electromagnetic action is therefore not necessary to explain the Hertz effects. Maxwell's theory, however, still remains of value and its truth is not gainsaid by the author.—Ann. der Physik und Chemie, No. 7, 1893, pp. 487–508. J. T.

12. Polarization of ultra red rays by means of metallic gratings. —H. E. J. G. DU BOIS and H. RUBENS have examined this subject by means of a bolometer which was inserted in the telescope of a suitable spectrometer. The amount of energy transmitted was measured in the two cases when the rays were polarized at right angles and also parallel to the gratings. The authors find a fruitful analogy between the polarization of the heat rays and the polarization of the electrical rays examined by Hertz.

13. Interference of electrical waves in air.—This has been shown by KLEMENCIC and CZERMAK in the following manner. A Hertz exciter was placed at the focus of a parabolic mirror and a resonator at the focus of a similar mirror. At the intersection of the axial lines of the mirrors could be slid two parallel plates of glass covered with tin foil. The apparatus, thus, was closely analogous to Fresnel's apparatus for showing by means of reflection from glass mirrors the interference of light waves. The mirrors having been placed side by side with the exciter at the focus of one and the resonator at the focus of the other, the two plates of glass covered with tin foil were moved parallel to each other along the intersection of the axes of the parabolic mirrors, until the proper difference of path of the waves necessary to produce interference was obtained. To detect resonance-a thermo-element connected with a suitable galvanometer was used. The results showed an interference phenomenon; but it was of a somewhat confused nature. - Ann. der Physik und Chemie, No. 9, 1893, pp. 174-188. J. T.

## II. GEOLOGY AND MINERALOGY.

1. Iowa Geological Survey, Vol. I. First Annual Report for 1892. 8vo, 472 pp., 10 plates and 26 figures. SAMUEL CALVIN State Geologist. Des Moines, 1893.—In addition to brief administrative reports, the first annual report of the Iowa Survey contains the following papers: Geological Formations of Iowa, Charles Rollin Keyes; Annotated Catalogue of Minerals, and Bibliography of Iowa Geology by same author; Cretaceous Deposits of Woodbury and Plymouth Counties, Samuel Calvin; Ancient Lava Flows in the Strata of Iowa, Samuel Beyer; Distribution and Relations of the St. Louis Limestone in Mahaska County, Harry Foster Baine; Some Niagara Lime-Burning Dolomites and Dolomitic Building Stones of Iowa, Gilbert L. Houser.

In discussing the classification of the geological formations of Iowa, Mr. Keyes has availed himself of the results of his own studies and those of others in recent years, and offers a classification that is a marked advance on those preceding it. With respect to Iowa's geological puzzle, the Sioux quartzite, some additional facts are noted which are presented in greater detail, however, in Mr. Beyer's paper. These relate to the discovery in a deep well at Hull, Iowa, of typical quartz-porphyry, an eruptive rock, in layers separated by beds of sand and pebbles presumably belonging to the Sioux quartzite. Reference is also made to the observations of Culver and Hobbs, showing the presence of intrusive sheets of eruptive rock within the quartzite in southeastern Dakota. The most probable explanation of the presence of the eruptive rock advanced by Mr. Beyer is that the sheets were intrusive lava flows from a post-carboniferous volcano. Considering the metamorphosing effect of eruptive rock it is to be questioned whether these rocks are as old as usually considered and Hayden's conclusion that they were Cretaceous is invested with new interest. We note the absence of such familiar names as Lower Magnesian, Potsdam, and Hamilton. The first is replaced by McGee's Oneota, the second by Winchell's St. Croix, while the attempt to correlate the Iowa Devonian with the New York section is wisely abandoned, and instead we have four sub-divisions, named from the place of their best development, the Independence Shales, the Cedar Valley Limestone, the Montpelier Sandstone, and the Lime Creek Shales. In defining the St. Louis group, on page 72, an error occurs in stating that the brecciated limestone is the basal member. Ten to twenty feet of magnesian limestone lie below this along the Des Moines river. The interesting and valuable discussion is given of the structure of the coal measures.

In Prof. Calvin's paper the Cretaceous deposits are shown to belong to the upper division and have a three-fold division corresponding to Meek and Hayden's Niobrara, Ft. Benton and Dakota. Much taste and care is shown in the make-up of the volume and the illustrations are exceptionally good. Acknowledgment should have been made to the Missouri Survey for the photograph for plate IX, as it was obtained by the writer while a member of that survey. C. H. G.

2. Note upon some observations on the auriferous Gravel of lacustral origin in the region of Taylorsville, California; by J. S. DILLER (from a letter to the editors, dated Aug. 28).— Recent observations show that to the southward the limit of the exposed area of lacustral gravels is the old shore line which has been much obscured by subsequent erosion; to the northward the gravels pass beneath the newer lavas of the Lassen Peak region and may extend far in that direction. Within, the area is chiefly occupied by smooth, round gravel. Where the gravel does not appear it has either been removed by erosion or is covered by later lavas or else was not originally deposited, as in the case of the islands. The gravel as now exposed, ranges in thickness from a few feet to over 400 feet. The pebbles of the older portion are of the auriferous slate series including old eruptive rocks, but the upper portion in many places especially along the beaches about the islands is composed largely of andesites and other later eruptives. Three islands of lava, chiefly volcanic breccia, have been noted; these are surrounded by beaches which in some cases are very well marked and not to be misunderstood. It is possible and even probable that the older gravels extend beneath the volcanic islands for the older gravels and the breccia are like those of the gravel channels farther south. At one point a dike is found in the gravels of which a large mass has been cemented so as to form conglomerate. In the Susanville region the gravels run beneath the Lahontan beds so they are of greater antiquity.

Originally the range in altitude of the gravels could not have exceeded a few hundred feet, but now they range from 4200 ft. on Gold Run to 7400 on the crest east of Diamond Peak a difference of 3200 feet. This difference as I have previously maintained (8th Annual Report) is due to displacement along the eastern escarpment of the Sierra Nevada. From the lower part of Gold Run near Susanville the smooth treeless gravel ridges and beaches on the crest of the range 3200 feet above, near Diamond Peak, are conspicuous. In the valley of Gold Run it is easy to distinguish between the gravel of that stream and the original lacustral deposits and the latter can be traced continuously from Diamond peak or mountain to near Susanville. The fault along Honey Lake runs out in an arch along Gold Run, and the Sierra Nevada ends to be succeeded by the volcanic cones of the Lassen Peak region.

I have already referred to the conglomerate cut by eruptives. It is at the head of Cheney Creek where the "conglomerate gravels" are bent down over the eastern slope. Gold Run follows close to the contact between the conglomerate and underlying diorite (or granite); the principal rock of that portion of the Sierra Nevada. That the conglomerate is only cemented auriferous gravel is shown by the fact that it grades into the gravel away from the particular eruptive which penetrates the mass. The pebbles and all features excepting degree of lithifaction are the same. The plants in both are essentially of the same age and in some cases identical species as determined by Ward and Lesquereux. The feature to which I wish in this connection to call attention is that where the fault runs into the arch and the conglomerate is bent over the eastern slope the pebbles are in many cases fractured and faulted. The argument in favor of displacement since the auriferous gravel period appears strong and conclusive.

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3. A Subtropical Miocene fauna in Arctic Siberia.—Dr. W. H. DALL, of the Smithsonian Institution, has given an interesting account (Proc. U. S. Nat. Mus., vol. xvi, pp. 471-478) of a small collection of Miocene fossils collected in 1855 by Dr. William Stimpson, on the shore of Penjinsk Bay, in the northeastern angle of Okhotsk Sea, at a small coaling station called by the whalers Coal Bay. The fossils were deposited in the Smithsonian and have only recently been described. The position assigned to Coal Bay on the map of the *Hancock's* expedition is latitude 60° 17' north, and longitude 161° 55' east, of Greenwich. The fauna described was a littoral fauna and presents analogy with those of the China and South Japan seas, and also indicates a bond of relationship with the west coast of Africa.

The present mean annual temperature of Okhotsk is  $23\cdot1^{\circ}$ , and the temperature of the sea water does not rise above  $40^{\circ}$  F. except in the harbor during the warmest part of the summer, and for two-thirds of the year it is at or below the freezing point. The annual mean temperature of the Gulf of Penjinsk indicated by the fossils, which are of Miocene age, as interpreted by F. B. Meek and also confirmed by Dr. Dall, "can not have been much less than  $60^{\circ}$  F. and was probably higher, that is to say since this fossil fauna flourished in these waters, the annual mean temperature has diminished by  $30^{\circ}$  to  $40^{\circ}$  F., at the most moderate calculation." Which fact the author concludes would be quite sufficient to prove that no polar conditions in the modern sense could have existed in eastern Siberia during the old Miocene epoch of geological time. H. S. W.

4. On the Glaciation of Asia.—In a paper before the recent meeting of the British Association, Prince Kropotkin summed up his knowledge on the general glaciation of Asia as follows: The Lowlands and Steppes, under 2000 feet in height, do not appear to have been glaciated; but all the mountain ridges rising over the Steppes, the great border ridges of Tian Shan and the Alpine tracts fringing the plateau, were covered with immense glaciers which descended to within 1000 feet of sea-level. The Viteni Plateau, the N. W. Mongolia Plateau, the Pamirs, and the great Khingim were extensively glaciated. The southern portion of the High Plateau, however, yield only indirect and not conclusive evidence of glaciation.—Nature, Sept. 28, 1893.

5. Two new localities for Turquoise; by W. E. HIDDEN (communicated).—The prehistoric group of turquoise mines in the Burro Mts.,\* of Grant County, New Mexico, which were first noticed publicly by Mr. Snow,† were visited by the writer in March of last year and the adjoining territory was looked into for other possible occurrences of turquoise. About fifteen miles southeast, some prospecting has been done for turquoise with some success; the locality is known as the Cow-Springs District. The matrix there is trachyte as in the Burros. In the same county

\* Now known as the Azure Mining Co. and at present being worked. They have produced as much as ten kilos. of fine turquoise in one month; mostly nodular and covered with a very peculiar "skin" or coating of silica (?).

+ This Journal, xli, 511, 1891.

and sixty miles in a southerly direction, turquoise has been found in many places, notably in and around Hachita. All the localities are prehistoric workings and similar in the method of occurrence to those in the Burros. The nearest railroad station is Separ, 22 miles north. All the surrounding region is very arid and desolate. The writer had eight weeks work done there last year and finally abandoned the region because of the scarcity of the blue shades of turquoise and the natural regional disadvantages (i. e., scarcity of water, etc.).

What I particularly wish to announce is the occurrence of turquoise, of fine color and quality, in a most unexpected locality, i. e., in the Jarilla Mts. of Doña Ana Co., some one hundred and fifty miles east of the Burros and two hundred miles south of the Los Cerillos region. Here again the discovery was due to the investigation of old-workings and the turquoise had passed as merely "copper-stain." The ancient pottery and stone implements which the writer caused to be unearthed there, proved the true character of the work and that the places had been abandoned for several hundred years. In the Jarillas, more than at Hachita, the aridity and isolation of the place becomes a very serious matter, since one must carry everything essential when visiting the mines. The nearest railroad station is Las Cruces, fifty miles west and El Paso, Tex., is about the same distance south (in an air line). The Jarillas are a low range of mountains about ten miles long and three miles wide (E. and W.) and rise up out of a wilderness of sand. They are uninhabited, except by a few wild animals, have no forest growths and no known springs of water. The well-watered and well-timbered "Sacramentos" are only 35 miles east, and it is but a day's journey from the desolate Jarillas to the habitable lands eastward or westward. The vegetation is scarce and mainly cacti and palmias. In spite of the isolation and the absence of water, a permanent mining camp\* has been established there and turquoise is being mined regularly. There are at least ten places where some tribe of people have worked for turquoise in past times, but all their work was very shallow and stopped whenever hard firm rock was encountered. Here the turquoise occurs in thin seams, cracks and crevices which have a nearly vertical position.

The trachyte is filled with long fissure-like cavities which are lined with minute crystals of quartz, upon which are implanted fine crystals of pyrite. Some cracks of the rock are filled with granular jarosite and gypsum coats some of the seams. A shaft seventy feet deep has been sunk on a contact with the porphyry and turquoise has been found all the way down. The associated minerals are limonite and kaolin at surface and at the bottom bright pyrite, chalcopyrite (rarely), gypsum, jarosite and kaolin.

\* Now known as the "Shoo-ar-mé Mine of the Jarillas."

† In one instance and at a distance of only 50 ft. from where turquoise was being mined, a vein of rich copper sulphide was found, and as a rare association some clear colorless crystals of wulfenite were observed that were hemimorphic and also pyramidally hemihedral.

No apatite could be seen in the trachyte and the writer suggests that the phosphoric acid may have been derived from the adjacent limestone which is fossiliferous and which may have capped this trachyte at no very distant day.

As the turquoise is found in its natural position, it gives strong evidence that the oxidation of the pyrite is the sole cause of the decomposition of the trachyte, etc., the cause also of the formation of the limonite, gypsum and jarosite and is itself a product formed subsequent to the kaolin. The kaolin is in one sense primary and the turquoise secondary, as its form and situation in the vein, crevice or pocket always proved. That all the turquoise was once kaolin was very evident. That the turquoise was the last mineral formed and was crystallized or grew amid the kaolin and was a gradual and direct alteration of it was positively shown in many ways. The majority of the turquoise masses are semi-globular or reniform in outline though compact masses are found wholly occupying small cavities and following exteriorly all the configuration of the "pockets." At one time I uncovered a surface of turquoise nodules nearly three feet square-some of it three-fourths of an inch thick-and the edges of the masses and nodules always terminated thickly and abruptly in the kaolin with a rounded minute botryoidal surface. While the tendency is towards blue in the Jarilla turquoise-more so than at any of the other places herein noted-there also occurs (rarely) in the surface veins, some very green varieties, some as green as chrysolyte rock. Any tendency towards green is an evidence of alteration.

Abundant as the turquoise is near the surface, it too, undergoes decomposition and sooner or later becomes white, soft and pulverulent. At depths below twenty-five feet the turquoise when first found is of a magnificent, almost ethereal, tint of blue, but this rapidly fades after it is detached from its matrix and becomes dry. I have seen it as deep blue as indigo and then fade gradually to a "robin's egg" shade. If after drying, turquoise adheres to the tongue it can be classed at once as of low grade and possessing little value. Where the rock is purest there the turquoise is found of best color, normal hardness and greatest durability. As the other "old workings" in the Jarillas become developed, it is thought that they will disclose turquoise as hard, as beautiful and as large, as the world has as yet seen. I state this advisedly from the fact that some fifty kilos of marketable turquoise was shipped from this locality in the first six months working and only one of the prehistoric mines was developed.

The Mexicans believe that both the "old Pueblos" and Aztecs worked these mines and it is true to-day that the Pueblos value turquoise—which they term "shoo ar-mé"—even more than the Navajoes. The Apachés call it "steh" and care little for it. The Mexican name for it is "char-chu-á-tey," which calls to mind the Aztec "chal-chi-hui-tl," of many authors.

#### III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. The North Polar Basin.—In an address delivered before the Geographical Section of the British Association, Mr. Henry Seebohm gives an interesting account of the sudden coming of summer in high latitudes from which the following paragraphs are quoted:

"The sudden arrival of summer on the Arctic Circle appears to occur nearly at the same date in all the great river basins, but the number of recorded observations is so small that the slight variation may possibly be seasonal and not local. The ice on the Mackenzie River is stated by one authority to have broken up on May 13th in latitude 62°, and by another on May 9th in latitude 17°. If the Mackenzie breaks up as fast as the Yenisei-that is to say, at the rate of a degree a day-an assumption which is supported by what little evidence can be found-then the difference between these two seasons would be nine days. My own experience has been that the ice of the Pechora breaks up ten days before that of the Yenisei, but as I have only witnessed one such event in each valley too much importance must not be attached to the dates. According to the Challenger tables of isothermal lines, the mean temperatures of January and July on the Arctic Circle in the valleys of the Mackenzie and the Yenisei scarcely differ, the summer temperature in each case being about 55° F., and that of winter  $-25^{\circ}$  F., a difference of 80° F.

On the American side of the Polar Basin summer comes almost as suddenly as it does on the Asiatic side, but the change appears to be less of the nature of a catastrophe. The geographical causes which produce this result are the smaller area of the river basins and the less amount of rainfall. There is only one large river which empties itself into the Arctic Ocean on the American side, the Mackenzie, with which may be associated the Saskatchewan, which discharges into Hudson Bay far away to the south. The basin of the Mackenzie is estimated at 590,000 square miles, whilst that of the Yenisei is supposed to be exactly twice that area. The comparative dimensions of the two summer floods are still more diminished by the difference in the quantity of snow. . . .

The arrival of summer in the Arctic regions happens so late that the inexperienced traveler may be excused for sometimes doubting whether it really is going to come at all. When continuous night has become continuous day without any perceptible approach to spring an alpine traveler naturally asks whether he has not reached the limit of perpetual snow. It is true that here and there a few bare patches are to be found on the steepest slopes, where most of the snow has been blown away by the wind, especially if these slopes face the south, where even an Arctic sun has more potency than it has elsewhere. It is also true that small flocks of little birds—at first snow-buntings and mealy redpoles, and later shore larks and Lapland buntings—may be observed to flit from one of these bare places to another looking for seeds or some other kind of food, but after all evidently finding most of it in the droppings of the peasants' horses on the hard snow-covered roads. The appearance of these little birds does not, however, give the same confidence in the eventual coming of summer to the Arctic naturalist as the arrival of the swallow or the cuckoo does to his brethren in sub-Arctic and subtropic climates. The four little birds just mentioned are only gipsy migrants that are perpetually flitting to and fro on the confines of the frost, continually being driven south by snowstorms, but ever ready to take advantage of the slightest thaw to press northwards again to their favorite Arctic home. They are all circumpolar in their distributions, are as common in Siberia as in Lapland, and range across Canada to Alaska as well as to Greenland. In sub-Arctic climates we only see them in winter, so that their appearance does not in the least degree suggest the arrival of summer to the traveler from the South.

The gradual rise in the level of the river inspires no more confidence in the final melting away of the snow and the disruption of the ice which supports it. In Siberia the rivers are so enormous that a rise of 5 or 6 feet is scarcely perceptible. The Yenisei is three miles wide at the Arctic circle, and as fast as it rises the open water at the margin freezes up again and is soon covered with the drifting snow. During the summer which I spent in the valley of the Yenisei we had six feet of snow on the ground until the first of June. To all intents and purposes it was mid-winter, illuminated for the nonce with what amounted to continuous daylight. The light was a little duller at midnight, but not so much so as during the occasional snowstorms that swept through the forest and drifted up the broad river bed. During the month of May there were a few signs of the possibility of some mitigation of the rigors of winter. Now and then there was a little rain, but it was always followed by frost. If it thawed one day it froze the next, and little or no impression was made on the snow. The most tangible sign of coming summer was an increase in the number of birds, but they were nearly all forest birds, which could enjoy the sunshine in the pines and birches, and which were by no means dependent on the melting away of the snow for their supply of food. Between May 16 and 30 we had more definite evidence of our being within bird flight of bare grass or open water. Migratory flocks of wild geese passed over our winter quarters, but if they were flying north one day they were flying south the next, proving beyond all doubt that their migration was premature. The geese evidently agreed with us that it ought to be summer, but it was as clear to the geese as to us that it really was winter.

We afterwards learnt that during the last ten days of May a tremendous battle had been raging 600 miles as the crow flies to the southward of our position on the Arctic Circle. Summer in league with the sun had been fighting winter and the north wind all along the line, and had been as hopelessly beaten everywhere as we were witnesses that it had been in our part of the river. At length, when the final victory of summer looked the most. hopeless, a change was made in the command of the forces. Summer entered into an alliance with the south wind. The sun retired in dudgeon to his tent behind the clouds, mists obscured the landscape, a soft south wind played gently on the snow, which melted under its all powerful influence like butter upon hot toast, the tide of battle was suddenly turned, the armies of winter soon vanished into thin water and beat a hasty retreat towards the pole. The effect on the great river was magical. Its thick armour of ice cracked with a loud noise like the rattling of thunder, every twenty-four hours it was lifted up a fathom above its former level, broken up, first into ice floes and then into pack ice, and marched down stream at least a hundred miles. Even at this great speed it was more than a fortnight before the last straggling ice-blocks passed our post of observation on the Arctic Circle, but during that time the river had risen 70 feet above its winter level, although it was three miles wide, and we were in the middle of a blazing hot summer, picking flowers of a hundred different kinds, and feasting upon wild ducks' eggs of various species. Birds abounded to an incredible extent. Between May 29 and June 18 I identified sixty-four species which I had not seen before the break up of the ice. Some of them stopped to breed and already had eggs, but many of them followed the retreating ice to the tundra, and we saw them no more until, many weeks afterwards, we had sailed down the river beyond the limit of forest growth.

The victory of the south wind was absolute, but not entirely uninterrupted. Occasionally the winter made a desperate stand against the sudden onrush of summer. The north wind rallied its beaten forces for days together, the clouds and the rain were driven back, and the half-melted snow frozen on the surface. But it was too late; there were many large patches of dark ground which rapidly absorbed the sun's heat; the snow melted under the frozen crust, and its final collapse was as rapid as it was complete.

In the basin of the Yenisei the average thickness of the snow at the end of winter is about five feet. The sudden transformation of this immense continent of snow, which lies as gently on the earth as an eider-down quilt upon a bed, into an ocean of water rushing madly down to the sea, tearing everything up that comes into its way, is a gigantic display of power compared with which an earthquake sinks into insignificance. It is difficult to imagine the chaos of water which must have deluged the country before the river beds were worn wide enough and deep enough to carry the water away as quickly as is the case now. . . .

The alternate marching of this immense quantity of ice up and down the Kureika was a most curious phenomenon. To see a strong current up stream for many hours is so contrary to all

previous experience of the behavior of rivers that one cannot help feeling continuous astonishment at the novel sight. The • monotony which might otherwise have intervened in a ten-days' march-past of ice was continually broken by complete changes in the scene. Sometimes the current was up-stream, sometimes it was down, and occasionally there was no current at all. Frequently the pack ice and ice floes were so closely jammed together that there was no apparent difficulty in scrambling across them, and occasionally the river was free from ice for a short time. At other times the river was thinly sprinkled over with ice blocks and little icebergs, which occasionally "calved" as they traveled on, with much commotion and splashing. The phenomenon technically called "calving" is curious, and sometimes quite startling. It takes place when a number of scattered ice blocks are quietly floating down stream. All at once a loud splash is heard as a huge lump of ice rises out of the water, evidently from a considerable depth, like a young whale coming up to breathe, noisily beats back the waves that the sudden upheaval has caused, and rocks to and fro for some time before it finally settles down to its floating level. There can be little doubt that what looks like a comparatively small ice block floating innocently along is really the top of a formidable iceberg, the greater part of which is a submerged mass of layers of ice piled one on the top of the other, and in many places very imperfectly frozen together. By some accident, perhaps by grounding on a hidden sandbank, perhaps by the water getting between the layers and thawing the few places where they are frozen together, the bottom layer becomes detached, escapes to the surface, and loudly asserts its commencement of an independent existence with the commotion in the water which generally proclaims the fact that an iceberg has calved.

Finally comes the last march-past of the beaten forces of winter, the ragtag and bobtail of the great Arctic army that comes straggling down the river when the campaign is all over—worn and weather-beaten little icebergs, dirty ice floes that look like floating sandbanks, and straggling pack ice in the last stages of consumption that looks strangely out of place under a burning sun between banks gay with the gayest flowers, amidst the buzz of mosquitoes, the music of song birds, and the harsh cries of gulls, divers, ducks, and sandpipers of various species."— *Geograph. Journal*, Oct., 1893.

2. An Elementary Treatise on Analytical Geometry; by W. J. JOHNSON, M.A. pp. 425, 8vo, 1893 (Macmillan and Co., London and New York.)—This volume is stated to be based upon, and designed as an introduction to, Salmon's well know mathematical series. For this purpose we are inclined to regard Salmon's conic sections as preferable; but the book will be acceptable to such as desire a limited course, selected paragraphs being marked out for their use accompanied by copious exercises.

### APPENDIX.

#### ART. LIV.—Description of Miocene Mammalia; by O. C. MARSH. (With Plates VII-X.)

THE object of the present article is to figure and to describe more fully a number of interesting remains of mammals which have already been named and briefly noticed by the writer. These specimens are mainly from the Rocky Mountain region, but a few were found on the Atlantic coast, in New Jersey, and, owing in part to this fact, it becomes possible for the first time to establish approximately in the Miocene a horizon common to the two regions.

#### Protoceras celer, Marsh.\*

The type specimen of this genus and species is represented, one-half natural size, in the two figures on the accompanying plate, number VII. Figure 1 represents the skull seen from above, and showing on the parietal bones (p) the diminutive horn-cores (h) that suggested the generic name. The suture (s) between the parietals and frontals (f) is very distinct in the specimen, and is clearly shown in the figure. The median elevation on the posterior part of the frontals is also well marked. The depression (a) in the maxillary is likewise a noticeable feature in this view of the skull.

In figure 2 of Plate VII, the same skull is represented as seen from below. This view shows the dentition to be ruminant in type, with the premolars all unlike the molars. The posterior nares (n) are noteworthy for their forward position.

The most interesting points in this type specimen were given by the writer in the original description above cited. The new genus *Protoceras* was shown to represent a distinct family, which was named the *Protoceratidæ*. Some characters seen in the type specimen suggested affinities with the Giraffes, and this fact was stated in the description.

In the following year, 1892, Dr. J. L. Wortman discovered several specimens of *Protoceras* in the same region where the type was found, and later Prof. H. F. Osborn and Dr. Wortman published an important paper on the genus, with figures, based upon this material.<sup>†</sup> These specimens proved that the type was the skull of a female, and that the male skull had, in addition to protuberances on the parietals, a pair

\* This Journal, vol. xli, p. 81, January, 1891.

<sup>+</sup> Bull. Amer. Mus., vol. iv, p. 351, 1892.

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, No. 275.-Nov., 1893.

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of elevations on the frontals, and a third pair on the maxillaries. With these were elongated canine tusks. The structure of the feet, also, was determined.

The horizon was subsequently stated to be a distinct one, just above the Oreodon beds, and was named by Wortman the "Protoceras beds."

In the Palaeontology of von Zittel (vol. iv, pp. 405-407), figures of the type specimen of *Protoceras* are given, reduced from the original drawings represented on Plate VII of the present article; also figures of the male skull and the feet, taken from Osborn and Wortman's paper.

#### Elotherium crassum, Marsh.\*

The type specimen of the present species was discovered by the writer in August, 1870, in the lower Miocene of Colorado, but was not described until 1873. It was found associated with a skeleton of *Brontotherium*, and thus its horizon was definitely determined. A second specimen was secured in the immediate vicinity, and in the same stratum. Researches in the same region during several succeeding years brought to light a number of other specimens, including several skulls and portions of the skeleton of this and other allied species.

Explorations begun by the writer in 1874, in Nebraska and Dakota, resulted in finding several additional specimens, and others have since been obtained in the same region during the explorations made for the U. S. Geological Survey. Still other very perfect specimens have been secured by the Yale Museum, so that now ample material is available for investigating both the present species and its near allies.

On Plate VIII of this article is represented, one-eighth natural size, a skull of *Elotherium crassum*, which is one of the most perfect ever discovered. The lower jaws are in place, and the nearly complete dentition is present and in fine condition. Figure 1 shows this skull as seen from the left side, with the jaws shut closely together, as found. One of the most noticeable features is the long dependent process (m)on the malar bone, which in this species extends downward to the inferior margin of the lower jaw, in front of the angle. This is the case when these processes are somewhat expanded transversely, as shown in figures 2 and 3, which represent the skull as it lay in the matrix. Another peculiar feature shown in figure 1 is the series of processes on the lower jaw, the first (a) being the dependent, everted angle of the ramus; the second (b) a protuberance under the third lower premolar; and the third (c) a process below the base of the canine. These processes are well shown, also, in figure 3.

\* This Journal, vol. v, p. 487, June, 1873.

Seen from above, in figure 2, the most noteworthy features are the small space occupied by the brain in the parietal region (p), the widely expanded malar processes (m), and the narrow, elongated facial portion. In this figure, the lower jaw is not represented. In figure 3, which shows the skull and lower jaws in position and seen from in front, many interesting points are shown. Copies of the original drawings of figures 1 and 2 will be found in von Zittel's Palæontology, Vol. IV, p. 337.

The feet of *Elotherium* have hitherto been known only imperfectly from fragmentary portions, but the extensive material already referred to has enabled the writer to make out their entire structure in the present species. In figures 4 and 5 of Plate VIII, the manus and pes are represented, one-sixth natural size. It will be seen that in each foot there are only two functional digits, corresponding to the third and fourth in man. The first digit is entirely wanting, and only remnants remain of the second and fifth.

#### Elotherium clavum, sp. nov.

On Plate IX, figure 1, is shown a skull of *Eiotherium*, with the brain cast in position, which agrees in many respects with the skull figured on the preceding plate, and described above. When first figured, the former skull was referred to *E. crassum* (Dinocerata, p. 65, 1884), but a more careful comparison proves it to be distinct. It is considerably smaller than *E. crassum*, and the malar process is quite slender and tapering below. It extends directly downward, and hence is not seen in the top view of the skull. The length of this skull is sixteen inches, measured from the front of the premaxillaries to the back of the occipital condyles. The dentition agrees, in the main, with that of *E. crassum*, the last lower molar in each having four cones only, and no heel. The malar arch and the dependent angle of the lower jaw will distinguish it from *E. Mortoni*. The type specimen here figured is from the Oreodon beds, near the White river, in southern Dakota.

#### Ammodon Leidyanum, gen. nov.

The teeth represented on Plate IX, figures 2 and 3, indicate a very large animal belonging to the same group as those last described, but differing in several respects. The first tooth, shown in figure 2, is the type specimen of *Elotherium Leidyanum*, already described by the writer.\* It is the fourth premolar of the right lower jaw, and was found in 1867, in a Miocene deposit in Monmouth county, N. J.

\* Proc. Phila. Acad., vol. xxii, p. 3; and Geology of New Jersey, p. 740, 1868.

#### 410 O. C. Marsh—Description of Miocene Mammalia.

The tooth represented in figure 3 is the last right molar, and was found at the same locality under circumstances which render it probable that it may have pertained to the same animal. The premolar agrees closely in form with the corresponding tooth in *Elotherium*, but the last lower molar, shown in figure 3, has, in addition to the four cones characteristic of *Elotherium*, a distinct fifth posterior cone, or heel, not present in typical specimens of that genus. The two genera represent a distinct family, which may be called the *Elotheridæ*.

#### Ammodon (Elotherium) bathrodon.\*

The type of the present species is the tooth shown on Plate IX, figure 4. It is the last lower molar of the right side, and, in its main features, agrees with the corresponding tooth last described. It indicates an animal somewhat smaller, but far exceeding in size most members of the group. Since this type specimen was described, two or three skulls of the same species have been secured by the writer, all found in the Miocene of Dakota, in the same general region where the type was discovered. These skulls agree in their general features with that of *Elotherium* figured on Plate VIII, but the braincase is proportionately larger, and the processes on the lower jaw are still more developed. The dependent angle of the lower jaw slopes backward, and not forward as in Elotherium crassum. The lower molar teeth, also, all have a posterior lobe more or less developed, and the last lower molar has a distinct heel. In one of these skulls, the space occupied by the upper premolar and molar teeth is twelve inches, and the space across the palate between the true molars is two and one-half inches.

#### Ammodon potens, sp. nov.

The present species is somewhat smaller than the one last described, and differs in having a proportionately more elongate skull and less robust teeth, especially in the molar series. All the lower true molars have a distinct posterior cone, and this is nearly as well developed on the first and second molars as on the last. The processes on the lower jaw are more elongate than in any other species of the group. The dependent process on the malar is also especially elongate. The space occupied by the lower premolar and molar series is twelve inches, and by the premolars alone seven and one-half inches. The depth of the lower jaw from the base of the canine to the end of the process below is seven and one-half inches, and the distance from the top of the fourth premolar to the end of the middle process below is seven inches.

The type specimen of the present species is from the Miocene of Colorado.

\* This Journal, vol. vii, p. 534, May, 1874.

#### Perchœrus (Dicotyles) antiquus.\*

On Plate X, figure 1, is shown a last upper molar tooth, which may be provisionally referred to the genus *Percharus* of Leidy. It is from the Miocene of Monmouth county, N. J., from the same locality where was found the lower molar tooth described by the writer as *Dicotyles antiquus*, and the two may be referred to the same species. The tooth is especially noteworthy in itself from the complicated structure of its crown, which approaches that seen in the existing suillines. The lower molar tooth, the type of the species, has a crown of simpler structure, and may be distinct.

#### Colodon luxatus, Marsh.†

The type specimen of the present genus and species is represented in part on Plate X, figures 2 and 3, which show the entire dentition of the lower jaw. In the original description cited above, it was shown that the present genus is probably nearly allied to *Lophiodon*, but could be readily distinguished from it by two inner cones on the upper premolars, and by the absence of canines in the lower jaw. The same characters and the presence of a posterior lobe on the last lower molar will separate it from *Hyrachyus*. The type specimen is from the Miocene of South Dakota.

#### Rhinoceros matutinus, Marsh.<sup>†</sup>

The lower molar tooth represented on Plate X, figure 4, is from the Miocene of Monmouth county, N. J., and was found in the same horizon and locality as the other specimens from New Jersey described above. Its main interest lies in this fact, the significance of which will be discussed later. The tooth is the last lower molar of the right side, and while the species appears to be distinct, the tooth agrees in its general structure with the corresponding molars of allied forms from the Rocky Mountains.

All the type specimens above described are preserved in the Yale Museum. These remains have a special interest when considered in connection with the localities in which they were found. Those from the West are from three definite horizons in the Miocene, lying one above the other on the eastern flank of the Rocky Mountains. Those from the Atlantic coast are all from a single horizon in the same formation, and this

\* Proc. Phila. Acad., vol. xxii, p. 11, 1870.

+ This Journal, vol. xxxix, p. 524, June, 1890.

<sup>‡</sup> Proc. Phila. Acad., vol. xxii, p. 3, 1870.

horizon, too, may now be sharply defined. The deposits containing the remains from New Jersey here described, and other vertebrate fossils obtained by the writer at the same or adjoining localities, form a well-defined stratum resting unconformably upon the Eocene greensand marls of Monmouth county, N. J. These Miocene deposits may be called the Ammodon beds, from the largest land animal hitherto found in them. So far as at present can be determined, this horizon corresponds most nearly to that in the Rocky Mountain region in which Ammodon bathrodon has been found. This subject will be discussed by the writer in a later communication.

Yale University, New Haven, Conn., October 24, 1893.

#### EXPLANATION OF PLATES.

#### PLATE VII.

FIGURE 1.-Skull of Protoceras celer, Marsh; seen from above.

FIGURE 2.- The same skull; seen from below. Both figures one-half natural size. a, depression in maxillary; f, frontal; h, horn-core; m, first molar; n, posterior nares; o, orbit; p, parietal; pm, second premolar; s, suture between frontal and parietal.

#### PLATE VIII.

FIGURE 1.-Skull of *Elotherium crassum*. Marsh; side view.

- FIGURE 2.- The same skull; seen from above.
- FIGURE 3.—The same skull; front view. These figures are onc-eighth natural size. a, angle of lower jaw; b, protuberance on margin of lower jaw; c, process below canine; f, frontal; m, malar process: mx, maxillary; n. nasal; p, parietal; pm, premaxillary; s, squamosal
- FIGURE 4.-Left fore foot of *Elotherium crassum*; front view.
- FIGURE 5 .- Left hind foot of same species; front view. Both figures are onesixth natural size.
  - a. astragalus; c, calcaneum; R, radius; U, ulna; II-V, digits and remnants of digits.

#### PLATE IX.

- FIGURE 1.-Skull of *Elotherium clavum*, Marsh, with brain-cast; top view. About one-fifth natural size.
- FIGURE 2.-Fourth lower premolar of Ammodon Leidyanum, Marsh. One-half natural size.
- FIGURE 3.-Last lower molar of same species. Also one-half natural size.
- FIGURE 4.-Last lower molar of Ammodon bathrodon, Marsh. One-half natural size.

#### PLATE X.

- FIGURE 1.—Last upper molar of *Perchærus antiquus*, Marsh. Natural size. FIGURE 2.—Left lower jaw of *Colodon luxatus*, Marsh; side view. One-half natural size.
- FIGURE 3.—The same jaw; seen from above.
- FIGURE 4.-Last lower molar of Rhinoceros matutinus, Marsh. One-half natural size.
- FIGURE 5.—Portion of lower jaw of Laopithecus robustus, Marsh. Natural size.

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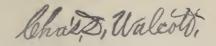
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#### [THIRD SERIES.]

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ART. LV.—On Endothermic Decompositions obtained by Pressure. Second Part. Transformations of Energy by Shearing Stress; by M. CAREY LEA.

OF the relations which exist between two forms of energy, mechanical and chemical, very little if anything is known. In the second volume of his Lehrbuch, Ostwald remarks that as to these relations "almost nothing" is known.\*

There are certain familiar cases in which mechanical energy may seem at first sight to be converted into chemical energy. The fulminates, iodimide, and other substances explode by shock. But it is hardly necessary to remark that all such reactions are exothermic and need an external impulse only, to start them—if this impulse were not needed such compounds could not exist at all. Were such reactions taken as true transformations of energy an absence of due relation between cause and effect would be involved. For the shock that suffices to explode a grain of fulminate will equally explode a ton. The faint spark that will explode a grain of gunpowder will also explode a magazine.

Present opinion holds undoubtedly that no true transformation of mechanical into chemical energy is known. Most text books do not consider the question at all. But Dr. Horstmann in the volume of theoretical chemistry which forms part of the last German edition of Graham Otto's Chemistry, discusses the

\* "Anderersetts ist von der Verhältnis zwischen mechanischer und chemischer Energie, fast nichts bekannt." A few lines below, this remark is repeated with emphasis. Lehrbuch, 2d German ed., vol. ii, p. 12.

AM. JOUR. SCI.—THIRD SERIES, VOL. XLVI, NO. 276.—DEC., 1893. 29 matter. His views are so much to the point that I shall translate a few sentences, putting in italics the statements to which I would specially refer.

"We must consequently admit that through a rough mechanical attack the molecular structure of certain chemical compounds can be disrupted and destroyed. This will certainly be possible only for compounds in whose molecules the arrangement of the atoms does not correspond to a stable equilibrium and in which therefore the chemical energies themselves are already striving to form simpler and more stable compounds out of the constituents of the existing substance. For it cannot be admitted that actual chemical changes can be brought about by a mechanical impulse." (l. c., p. 350).

In another chapter he says with equal distinctness :

"By mechanical means alone no reaction against the force of chemical energy can be brought about. By a shock or blow the molecular structure of chemical compounds can indeed be so far loosened that free play is given to chemical forces; but against these forces we cannot by mechanical means separate the atoms nor combine them in a definite way." (p. 594).

These expressions of a distinguished chemist will sufficiently indicate what has been up to the present time the opinion of chemists as to the possibility of transforming mechanical energy into chemical.

In the first part of this paper I believe I have been able to show in a qualitative way the production of true endothermic reactions by mechanical force. In the present part I hope to show an increased number of such reactions and in one case to exhibit actual quantitative results, at least so far as to obtain the product of the transformation in weighable quantities.

In the first part decompositions were described that were brought about by *simple pressure*. Compounds formed by exothermic reactions, and therefore requiring expenditure of energy to break them up, were decomposed. The investigation might probably have been made to include a still larger range of substances. But it was found that the efficiency of pressure was so enormously increased by the addition of shearing motion, that decompositions requiring a force of hundreds of thousands of pounds with pressure alone, could be effected by the mere strength of the hand when shearing stress was used. More than this, decompositions which enormous pressures failed to effect, readily took place under the action of shearing stress.\*

\* It would not have been difficult to obtain much greater pressures than those described in the first part of this paper. This could be effected by means of the differential screw. I had planned for a screw with threads of 40 turns in 10 inches

 $(\mathbf{I})$ 

It was mentioned in a previous paper on the decomposition of the silver haloids by mechanical force that when silver chloride was sharply ground for some time in a mortar, both the pestle and mortar became covered with a deep purple varnish of silver photochloride, thus indicating a partial reduction to subchloride. It has since proved that there is no more effectual method than this of applying shearing stress and that in this way a number of quite stable chemical compounds formed by exothermic reactions can be broken up. The mortar and pestle should be very solid and of unglazed porcelain. With metal, there would be danger of action between the metal and the substance and with agate mortars sufficient force cannot well be applied. In many cases success depends on the exertion of great pressure on the pestle. It is also absolutely essential that the quantity of material acted upon should be small. When a larger quantity is employed the particles slip or roll over each other and thus escape the action of the stress. It is no doubt for this reason that the very remarkable results which can be obtained in this way have hitherto escaped attention.

A small quantity, a few decigrams, of the substance having been placed in the mortar the first thing is to spread it in a thin uniform coat over the bottom and part of the sides. The pestle is then to be rotated with the utmost force that can be exerted.

Sodium Chloraurate.—The salts of gold are particularly well adapted to this examination as the reduction is complete

and  $39\frac{1}{2}$  turns in 10 inches respectively. The mechanical efficiency of such a screw is that of one having 320 turns to the inch if such a thing were practicable, at the same time that a thoroughly strong construction can be obtained. The massive steel nut to advance  $\frac{1}{2}$  of an inch would require 40 full turns of this screw.

This arrangement compares as follows with that previously employed. In it to cause the vise jaws to approach by 1 inch required that the point of the lever at which the force was applied should pass through a space of  $113^{\circ}1$  feet: this relation. 1 inch to  $113^{\circ}1$  feet or  $1:1357^{\circ}2$  gives the measure of the efficiency of the instrument.

With the double screw, on the other hand, to cause the nut to advance  $\frac{1}{3}$  of an inch the end of the lever (2 feet long) must pass through a space of 500 feet or in the proportion of 1 inch to over  $\frac{3}{4}$  of a mile. The circumference described by the lever being approximately  $12\frac{1}{2}$  feet and the screw requiring 40 turns to advance the nut  $\frac{1}{3}$  of an inch we get the proportion of 1 inch to 4,000 feet, or 1 to 48,000, which is the measure of the efficiency of such an instrument. Therefore, supposing two men to pull on the end of the lever each with a pull of 100 lbs. the pressure exerted on the nut (disregarding loss by friction) would be 9,600,000 lbs., which could be doubled by using a 4-foot lever.

Such a combination is quite practicable, the only real difficulty being to obtain sufficient solidity of construction to resist the strain. I had made drawings for this instrument, but gave it up in consequence of observing the enormously greater efficiency of shearing stress as a means of transforming mechanical into chemical energy. and the gold appears in the metallic state so that it can be weighed and the exact amount of reduction can be fixed. It will be seen by (3) below that it may amount to as much as over 4 per cent of the gold present.

(1) Two or three decigrams of chloraurate with a moderate trituration left 1.8 milligram of metallic gold. Under the action of the pestle the yellow color of the salt gradually deepened to an olive shade. When water was poured on, the undecomposed salt dissolved, leaving the gold as a delicate purple powder. The color of the gold being purple instead of the more usual brown shade explains the olive color just mentioned, yellow and purple combining to form olive.

(2) Half a gram of the salt was taken. This specimen was more neutral than the preceding and was therefore more easily reduced. Half an hour's trituration had for effect the reduction of 9.2 mgs. of gold.

(3) A similar treatment of the same quantity of chloraurate resulted in the separation of 10.5 mgs. of gold.

These may seem at first somewhat small proportions. But it is to be recollected that the force is necessarily applied at a disadvantage and that the equivalent in work of chemical affinity is always very large. In the present case the figures are as follows: Thomsen found as the heat equivalent for the combination of gold with chlorine to form auric chloride 28.8 great calories. Taking the atomic weight of gold as 197, we find that one gram of gold in forming auric chloride disengages 115.7 small calories or water-gram-degrees, whose equivalent, taking Rowland's determination, is 49,288.2 gram-meters corresponding to  $4.83 \times 10^{\circ}$  ergs or 483 joules.

The small quantity of gold reduced in (3), 10<sup>1</sup>/<sub>2</sub> milligrams, would by conversion to auric chloride generate 1.215 watergram-degrees of heat whose equivalent in work is 518 grammeters. As heat is a degraded form of energy such an actual transformation without loss to a higher form would be impossible. It is more correct to say, therefore, that the amount of energy which would raise 518 grams to the height of one meter can be transformed into the same amount of heat, 1.215 water-gram-degrees, as is evolved by 10.5 mgs. of gold by conversion into auric chloride. Consequently this work, 518 grammeters represents the amount of mechanical energy transformed into chemical energy in operation [3].\*

It does not appear that in effecting these reactions and the others which remain to be described, mechanical energy under-

<sup>\*</sup> The amount of energy required would in fact slightly exceed this as the thermochemical equivalent of formation of sodium chloraurate would slightly exceed that of auric chloride. For the chloraurate I do not find a determination, but preferred to use this salt in the operation as being both more stable and more neutral, than auric chloride.

#### M. C. Lea—Endothermic Decompositions by Pressure. 417

goes an intermediate conversion into heat. Rapid movements are not needed, what is required is strong pressure with movement, but this need not be rapid. Nor does the mortar or the pestle become sensibly warm. The operation does not need to be continuous but may be broken up with any number of intervals. But a decisive conclusion can be drawn from those cases in which decompositions are effected in this way that *cannot be produced by heat*. For example, in the next instance to be mentioned there is a partial reduction of corrosive sublimate to calomel. By heat, corrosive sublimate sublimes unaltered and the same is true of mercurous chloride. The three silver haloids fuse unchanged at a red heat. The same conclusion can be drawn from other reactions.

These results were obtained in an atmosphere absolutely free from dust so that the reducing action of this substance was completely excluded.

Mercuric Chloride.—A specimen which after lightly powdering did not darken in the least with ammonia, was triturated in the manner just described with several intervals, in all for 15 minutes. It then became gray in a very striking way when moistened with ammonia.

This is a very interesting reaction. In the first part of this paper it was mentioned that mercuric chloride could be subjected to a pressure of about 70,000 atmospheres absolutely without change. It appears, however, that a pressure amounting to less than a hundred pounds causes decomposition when combined with movement, showing the enormously greater efficiency of shearing stress as compared with simple pressure. Not only this but as just mentioned shearing stress produces decompositions which heat is not competent to effect.

*Mercurous Chloride.*—When calomel was sharply triturated in a mortar it first became yellow and then blackened without difficulty.

Turpeth Mineral, 3HgO, SO<sub>3</sub>.—Reduces rather slowly.

*Mercuric Oxychloride*, 2HgO, HgCl<sub>2</sub>, obtained by precipitating corrosive sublimate by potash acid carbonate, exhibited the following reaction. Its brownish purple color by light grinding became lighter and then when strong force was used it blackened with remarkable ease.

Mercuric Iodide shows a trace of blackening.

*Mercuric Oxide.*—This substance yields much more readily to trituration than to simple pressure. Especially on the sides of the mortar it was quite blackened. The layer of material must be quite thin otherwise little effect is produced.

*Platinic Chloride.*—Gradually darkened in a very marked way, finally becoming blackish.

Ammonium Platinichloride gave same result.

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Silver Tartrate.—When spread in a very thin skin over the mortar each sharp stroke of the pestle left a black line behind it. This is a strong constrast with the complete resistance of this substance to simple pressure.

Silver Carbonate.—Action similar.

Silver Citrate.—Blackens very easily.

Silver Oxalate.—At least as easily.

Silver Arsenate.—Nearly as easily.

Silver Sulphite.—Effect visible in five minutes and gradually increasing. Very well marked.

Silver Salicylate.—No silver salt appears to be so easily reducible as this. Every sharp stroke of the pestle leaves a brown mark behind it.

Silver Orthophosphate.—Affected easily. After the phosphate has been a good deal reduced the unchanged part may be dissolved out with ammonia. The black residue after washing readily dissolves in dilute nitric acid and the solution gives a white cloud with hydrochloric acid.

Potassium Ferridcyanide. — A crystal of the pure salt sharply ground in a mortar becomes in portions brown and in others blue. The quantity used must, as indeed in all of the above cases, be small, one or two decigrams. If a little distilled water be added an insoluble blue powder is left behind and the solution formed strikes a blue color when added to one of ferric alum. This indicates that the decomposition is twofold. The experiment is quite a striking one and the result is easily obtained.

#### (II)

This form of mechanical force, shearing stress, may be applied to effect endothermic change in other ways. A very simple, and at the same time very efficient, method is that of pressure with a glass rod. Pure strong paper is to be imbued with a solution of the substance, if it is soluble, or if not, it is to be made into a paste with water and then applied with a brush. The paper is to be then very thoroughly dried and is to be laid upon a piece of plate glass. Characters are to be marked on it with the end of a glass rod that has been rounded by heat, using as much pressure as is possible without tearing the paper.

More than twenty years ago I was able to show that marks made in this way on sensitive photographic films could be developed, as an invisible image had been impressed. That, however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod, a result which may be obtained with various salts of gold, mercury, silver and other metals.

#### M. C. Lea-Endothermic Decompositions by Pressure. 419

Potassium Ferrideyanide.—Pure paper was imbued with a dilute solution of this salt. After thorough drying it was laid on a glass plate and marks were made with a glass rod in the manner just described. These marks were immediately visible and when the paper was plunged into dilute solution of ferric ammonia alum or of ferric chloride they became dark blue. It is probable that the decomposition here effected was twofold (see above).—The *nitroprussides* appear to be much more stable than the ferrideyanides. When sodium nitro prusside paper was treated with pressure, followed by appropriate reagents, no indications of decomposition were obtained.

Auric Chloride.—Paper imbued with a solution of auric chloride and marked in the manner described was thoroughly soaked in water to remove, as far as possible, the rest of the gold salt. The marks were very distinct and gradually gained with time. Color dark purplish gray.

Platinic Chloride.—After drying and marking, the paper was thoroughly soaked in water and dried. The marks were very distinct, of a yellow color.

Ammonium Platinichloride.—Marks very visible. Continued to slowly deepen, and in a few weeks were almost black.

Silver Carbonate. — The traces of the rod were brown. When the paper was placed in ammonia the carbonate dissolved, but the marks resisted the action of the ammonia and remained.

Silver Phosphate.—Action very similar to the preceding.

Silver Arsenate.-Similar action.

Silver Tartrate and Oxalate.—These salts gave analogous results to the preceding, but not so well marked. The carbonate phosphate and arsenate show this reaction best and about equally well. What is rather curious is that silver chloride does not exhibit a visible action.

Mercuric Oxide.—Paper imbued with a saturated solution of mercuric nitrate and then treated with solution of potash and dried shows this reaction very distinctly. Mercuric oxide appears to be quite sensitive to light.

Turpeth Mineral.—Mercuric sulphate was dissolved in water with the aid of sulphuric acid. Paper was soaked in the solution, allowed to become nearly dry and then washed. This paper showed the reaction very moderately, but the marks were brought out more strongly by immersion in ammonia.

*Ferric Alum (ammonia).*—Paper imbued with solution of this salt dried and marked was immersed in solution of potassium ferrideyanide. The marks came out blue showing that the ferric salt had undergone partial reduction.

It is easily conceivable that the action of shearing stress should be enormously greater than that of simple pressure. For it seems probable that pressure can only cause decomposition when the resulting product is more dense, has a greater specific mass, than the original substance. With shearing stress the case is altogether different. All matter is in a state of vibration and it is easily conceivable that the forcible friction of a hard substance may increase vibration in somewhat the same way as does a bow drawn over a stretched cord. Both the elasticity and the tension of the atoms themselves are vastly greater than those of any stretched cord so that the increased vibration may easily be sufficient to shatter the molecule.

The transformation of light, heat, and electricity into mechanical energy as well as the converse transformations are extremely familiar. That mechanical energy may be transformed into chemical energy is proved by the results in these papers described. The converse transformation, that of chemism into work, is in an industrial point of view by far the greatest chemical problem now waiting for solution. But it is by no means certain that such a transformation is practically possible. At least it seems probable that the improvement in our method of obtaining work from the chemism of carbon may be in the direction of substituting electricity for heat as the intermediary.

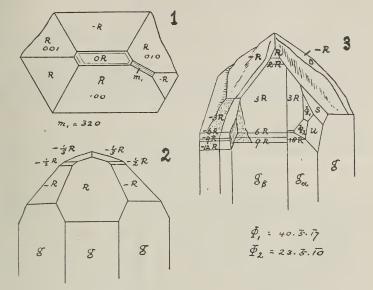
#### ART. LVI.—Quartz from the Emerald and Hiddenite Mine, North Carolina; by H. A. MIERS

THE remarkable crystals of quartz from this locality have been the subject of several memoirs by the late Professor G. vom Rath, which render it unnecessary to say anything regarding the general features of the North Carolina quartz. The following note, which relates to three interesting crystals recently presented to the British Museum by Mr. W. E. Hidden, serves to confirm and supplement the observations of vom Rath, concerning the rare planes which occur upon some of the more highly modified crystals from the Hiddenite mine. In the accompanying diagrams the crystals are drawn and lettered in accordance with the position and notation adopted by vom Rath in order to facilitate reference to his figures.

Crystal No. 1 is remarkable as showing a very well developed basal plane (fig. 1); the crystal is a pyramid R, -R, broken at its lower end so that no prism faces are visible; the

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apex is truncated by a smooth face which is certainly as perfect an example of the basal plane upon quartz as any which exist. The face is dull and slightly rounded, and the central portion is slightly raised above the edges as indicated in the figure, but it is sufficiently smooth to yield an image on the



reflecting goniometer. Measurement in the zone  $R: -R = [100:\overline{1}22]$  gave a series of images occupying an angular breadth of about  $3\frac{1}{2}^{\circ}$ :

This face has all the appearance of a corrosion surface and I share the opinion of Molengraaf that most of the rare planes upon the North Carolina quartz have been produced in this way.

The crystal is further remarkable for one of the very rare planes which replace the edges of the primary rhombohedron; only one such edge is developed in the present instance and it is replaced by a face m which is rounded in the zone RR.

This surface yields a series of somewhat indistinct images in the zone RR which correspond to the following inclinations to (100).

hk0:	100	$\frac{h+k}{1-1}$
31°	34'	$\begin{array}{c} h-k\\ 4.64 \end{array}$
31	59	4.82
32	26	5.03
32	54	5.28
34	3	5.98
34	47	6.52

The first four images are the best; the angle RR was measured as  $85^{\circ} 45^{3}_{4'}$ .

This face or corrosion surface is doubtless identical with that described by vom Rath\* from the same locality as a right hemi-scalenohedron replacing the edge RR, and accompanied by  $-\frac{1}{2}R = \{110\}$ , the symbol being  $-\frac{11}{18}P\frac{11}{7} = \{11.7.0\} = \{4.7.\overline{11}.18\}$ .

The above measurements show that the face may with greater probability be referred to the form  $\{320\} = -\frac{3}{5}P_3^2 = \{12\overline{3}5\}$  for which the angle is  $100:320 = 32^{\circ}23\frac{1}{2}', \left(\frac{h+k}{h-k}=5\right)$ . The angle measured by vom Rath was  $31^{\circ}$  13' (approximate). The order of the rhombohedral axes adopted here is such as to harmonize with the indices of previous authors who have used the Millerian system in describing new faces on quartz.

Crystal No. 2 exhibits a very unusual habit (fig. 2), being terminated by three large and well-developed faces of the obtuse rhombohedron  $-\frac{1}{3}R = \{441\}$  which gives it the aspect of a calcite termination. This extremely rare face was observed by vom Rath on a curious crystal from the same locality (Zeitschr. f. Krystallographie, x, 170, Taf. vi, fig. 5). There, as in the present instance, the form  $-\frac{1}{3}R$  is accompanied by small planes of  $-\frac{1}{2}R$  which truncate the edges of the primary rhombohedron; but the measurements of vom Rath were insufficient to establish the symbols with certainty.

On the crystal represented in fig. 2 the faces of  $-\frac{1}{3}R$  are dull and drusy as though due to a corrosion which has also spread partly over the small faces of  $-\frac{1}{2}R$ ; the latter are otherwise smooth and reflect well; the inclinations of  $-\frac{1}{3}R$ can be measured with perfect accuracy after the faces have been slightly oiled.

	Measured.	Calculated.
$-R:-\frac{1}{2}R =$	$19^{\circ} 21'$	$19^{\circ} 22'$
$-R:-\frac{1}{3}R$	$28 \ 48$	28.50

Crystal No. 3.—This crystal, represented in fig. 3, is interesting on account of two faces  $\Phi_1 \Phi_2$  which are right positive hemiscálenohedra lying out of the usual zone Rsu.

\* Zeitschr. f. Krystallographie, x, 172.

H. A. Miers—Quartz from North Carolina.

The crystal is somewhat difficult of measurement on account of the uneven nature of the principal rhombohedron faces, and the usual horizontal striæ and vertical reëntrant angles upon the prism.

The faces -R of the figure are curved and only retain a small plane surface near their right-hand edges which yields a brilliant reflection belonging to -R. The prism faces  $g_{\beta} g_{a}$  make a reëntrant angle of 0°  $20\frac{1}{2}'$  but  $g_{a}$  is inclined at 59° 59' to q.

The indices of  $\Phi_1$  and  $\Phi_2$  can therefore be best fixed by measuring the inclinations of these faces to  $g_a g_\beta s$  and u; care being taken to employ the right hand portion of 3R, since this face has a vertical reëntrant angle (indicated in the figure) of 0° 16'.

The form  $\Phi_1$  has been observed by vom Rath on similar crystals from this locality (Zeitschr. f. Krystallographie, xii, 453, Taf. viii, fig. 1) and has the symbol

$$40.\overline{5}.\overline{17} = \frac{19}{6}P_{\frac{19}{5}} = 15.4.\overline{19}.6$$

established without any doubt by the following measurements :

	Measured.	vom Rath.	Calculated.
$3R: \Phi_1 = -$	11° 9′	$10^{\circ} 57' - 10^{\circ} 50'$	$11^{\circ} 8\frac{1}{4}'$
$s: \Phi_1$	$19 \ 33$	19 54 - 19 56	$19 \ 38\frac{3}{4}$
$u: \Phi_1$	3 51	$3^{\circ} 57$	3 43
$g_a: \Phi_1$	$19 \ 12$		$19 \ 1$
$g: \varPhi_{_1}$	50 16		$50 \ 14$

The face  $\Phi_{a}$  presents somewhat greater difficulty; it yielded the following measurements:

			ted for
	Measured.	$\Phi_2 = 23.\overline{5}.\overline{10}$	$\Phi_2 = 32.\overline{7}.\overline{14}$
$3R: \Phi_2 =$	$8^{\circ} 26'$	$8^{\circ} 30\frac{1}{4}'$	$8^{\circ} 34\frac{1}{4}'$
$s: \Phi_2$	$24 \ 25\frac{1}{2}$	24 27	$24 \ 30\frac{1}{4}$
$u: \Phi_2$	5 57	$5 44\frac{1}{4}$	$5 43\frac{1}{4}$
$g_a: \Phi_2$	14 4	$14 \ 4\frac{1}{4}$	13 58
$g: \Phi_{_2}$	52 18	$52 \ 49\frac{1}{2}$	$52 \ 46$

The measurements suggest as the simplest symbol:

$$\Phi_{3} = 23.\overline{5}.\overline{10} = \frac{33}{8}P\frac{33}{58} = 28.5.\overline{33}.8$$

With indices of such complexity, however, which seem to be scarcely subject to the law of rationality it is important to ascertain whether a slight change of the numbers will not bring the position of the face into harmony with others of the rare trapezohedra of quartz.

Now  $\Phi_s$  lies almost in the same zone with s and two planes recorded by Des Cloizeaux in his classic memoir on quartz (pp. 107, 118) namely: 424 H. A. Miers—Quartz from North Carolina.

$$\begin{array}{l} \Pi = 18.\overline{3}, \ \overline{8} = \frac{26}{7} P \frac{26}{21} \\ \Phi = 25.\overline{5}.\overline{1}\overline{1} = \frac{18}{5} P \frac{6}{5} \end{array}$$

The former replaces the edge between u and 3R on a crystal from Wallis (fig. 27); the latter replaces the edge between sand an acute rhombohedron to which the symbol 8R is ascribed, on a crystal from Wallis (fig. 41); both forms are, it is true, somewhat doubtful, and no numerical measurements are given for the face  $\Phi$ ; it is in fact quite possible that the latter may be identical with  $\Phi_s$  of the present crystal.

If  $\Phi_s$  belongs to the zone  $s\Pi$  it must have the symbol:

$$32.\overline{7}.\overline{14} = \frac{46}{11}P\frac{46}{39} = 39.7.\overline{46}.11$$

The angular values corresponding to this symbol are given in the last column of the preceding table and approximate very closely to the observed angles; in fact it is scarcely possible from the above observations alone to distinguish between the two symbols.

Now the measurements are perfectly reliable, both  $\Phi_1$  and  $\Phi_2$  being bright faces which yield very sharp reflexions.  $\Phi_1$  is smooth, and  $\Phi_2$  is slightly striated in a direction almost coincident with the edge  $\Phi_1 \Phi_2$ 

In order to establish with accuracy the zone  $\Phi_1 \Phi_2$  we may seek to determine the acute rhombohedron which it contains.

Between 3R, which is a brilliant face, and the prism  $g_a$  is an acute rhombohedron  $Y_1$ .

Now since the angle  $3R : g_a$  differs by  $15\frac{1}{2}$ ' from its calculated value, and the face 3R yields the better reflection and is free from striations, we must determine the indices of  $Y_1$  from its inclination to 3R, disregarding  $g_a$ . Hence

 $Y_1 = 18R$   $3R : 18R = 12^{\circ} 14\frac{1}{2}'$  (calculated).

Assuming the indices

 $\Phi_1 = 40.5.1\overline{7}, \ \Phi_2 = 23.5.1\overline{0}$ 

the zone  $\Phi_1 \Phi_2$  contains the rhombohedron  $76.\overline{35}.\overline{35} = \frac{37}{2}R$ which is inclined to 3R at the angle  $12^{\circ} 16\frac{1}{2}$  and therefore practically coincides with  $Y_1$ .

If, on the other hand the indices of  $\Phi_s$  are  $32.\overline{7}.\overline{14}$  the zone  $\Phi_1 \Phi_2$  contains the rhombohedron  $104.\overline{49}.\overline{49} = \frac{5}{2}R$  which is inclined to 3R at the angle  $12^{\circ}$   $56\frac{1}{2}$ .

Hence there can be no doubt that the symbol of the new face is

$$\Phi_{2} = 23.\overline{5}.\overline{10}$$

Wells and Walden—Double Chlorides, Bromides, etc. 425

#### ART. LVII.—On the Double Chlorides, Bromides and Iodides of Casium and Cadmium; by H. L. WELLS and P. T. WALDEN.

SINCE the cæsium mercuric halides\* had been studied by one of us with the result that six types of double salts were found, it seemed desirable to extend the investigation to the metal cadmium on account of its close relation to mercury. We have, therefore, undertaken this work and as the result of a systematic and very thorough search have obtained the following compounds. The salt Cs<sub>2</sub>CdCl<sub>4</sub> had already been described by Godeffroy.

3:1 Type.	2:1 Type.	1:1 Type.
	Cs CdCl	CsCdCl.
Cs <sub>s</sub> CdBr <sub>s</sub>	Cs CdBr	CsCdBr,
Cs <sub>3</sub> CdI <sub>5</sub>	Cs <sup>°</sup> <sub>a</sub> CdI <sup>°</sup>	CsCdI, H <sub>2</sub> O

These cadmium salts correspond to the three types of mercuric compounds which contain the largest proportion of cæsium, and no evidence of the existence of cadmium double halides analogous to the 2:3, 1:2, and 1:5 types of cæsium-mercuric salts could be obtained. It is evident that the tendency to form a variety of double halides decreases from mercury to cadmium.

Three types of cadmium double halides with alkali metals and ammonium have been previously described, and a list of these is as follows:

4:1 Type.	2:1 Type.	1:1 Type.
(NH <sub>4</sub> ) <sub>4</sub> CdCl <sub>6</sub>	(NH <sub>4</sub> ) <sub>2</sub> CdCl <sub>4</sub> . H <sub>2</sub> O	KCdCl <sub>a</sub> . <sup>1</sup> / <sub>2</sub> H <sub>a</sub> O
K <sub>4</sub> CdCl <sub>6</sub>	Na CdCl . 3H O	NaCdBr, $2\frac{1}{2}$ H,O
(NH <sub>4</sub> ) <sub>4</sub> CdBr <sub>6</sub>	K <sub>2</sub> ČdCl <sub>4</sub>	KCdBr, H2H2O
K4CdBr	K <sub>2</sub> CdCl <sub>4</sub> .H <sub>2</sub> O	NH4CdBr3. H2O
	$(NH_4)_2CdI_4.2H_2O$	$\rm NH_4CdF_8$
	$Na_2CdI_4.6H_2O$	
	$K_2 C dI_4$ . $2 H_2 O$	

It is noticeable that, while the 2:1 and 1:1 salts in the above table correspond to two types of the cæsium salts which we have prepared, the 4:1 type of ammonium and potassium compounds differs from our 3:1 cæsium-cadmium salts and from the corresponding cæsium-mercuric compounds. We were entirely confident that our results were correct, for the salts were well crystallized and carefully prepared for analysis, and it was impossible to believe that we had obtained too little

\* This Journal, III, xliv, 221.

cæsiùm in our analyses, because the salts of this type were crystallized from solutions containing a large excess of cæsium halide. In order to convince ourselves that there was no mistake about the 4:1 formulæ we have prepared the two chlorides according to the directions of von Hauer who described them. The salts were extremely well crystallized and it was easy to obtain them in a very pure condition. The results of the analyses were as follows:

	Fou	nd.	Calculated for $K_4$ CdCl <sub>6</sub> .
Potassium	32.35		32.49
Cadmium	23.39	23.36	23.27
Chlorine	44.00	44.12	44.24
	Fou	nd.	Calculated for $(NH_4)_4 CdCl_6$ .
Ammonium		nd.	
Ammonium Cadmium	18.20		$(\mathrm{NH}_4)_4 \mathrm{CdCl}_6.$

These results confirm von Hauer's formulæ, and the curious fact must be accepted that cæsium forms 3:1 double halides with cadmium, while potassium and ammonium form salts of the 4:1 type.

The four types of cadmium double halides now known form a very simple and symmetrical series, the ratios of the alkalimetal to cadmium being 4:1, 3:1, 2:1 and 1:1. The first two of these types do not conform to Remsen's so-called law\* concerning the composition of double halides.

Preparation and General Properties.—The compounds to be described were prepared by making warm solutions of the component halides, and after concentrating if necessary, cooling to crystallization. Water, slightly acidified with the corresponding acid to prevent the formation of basic compounds, was used as the solvent, and in one instance, where a solution became syrupy from a large excess of a cadmium salt, alcohol was also tried, but without any advantage. The conditions were varied gradually in each case all the way from the point where the solution was saturated with the cæsium halide to the point where it was saturated with the cadmium halide, and so many experiments were made that we believe that no double salt, capable of existence at the temperatures used, was overlooked. It was noticed that variations in the concentration of any given solution had little effect upon the identity of the salt produced. In this respect the cadmium compounds differ considerably from those of mercury, for with the latter,

\* Am. Chem. Jour., xi, 291.

concentration is often an important factor in determining the salt produced.

The three 1:1 compounds CsCdCl<sub>s</sub>, CsCdBr<sub>s</sub> and CsCdI<sub>s</sub>. H<sub>2</sub>O and also the 2:1 iodide Cs<sub>2</sub>CdI<sub>4</sub> are capable of being recrystallized from water unchanged. The salt Cs<sub>2</sub>CdCl<sub>s</sub>, when dissolved in water, yields CsCdCl<sub>s</sub>, the two bromides Cs<sub>2</sub>CdBr<sub>s</sub> and Cs<sub>2</sub>CdBr<sub>4</sub> yield CsCdBr<sub>5</sub> while the iodide Cs<sub>3</sub>CdI<sub>5</sub> gives Cs<sub>2</sub>CdI<sub>4</sub>. These facts show that the salts having the larger proportions of cæsium require the presence of an excess of cæsium halide for their formation. The 1:1 salts all crystallize unchanged from extremely concentrated solutions of the corresponding cadmium halides.

All the salts are colorless. A pale violet color noticed in a few crops of the bromide  $Cs_2CdBr_4$  is supposed to have been due to some unknown foreign substance.

The solubility of the analogous salts in water or in saline solutions evidently increases from the chlorides to the iodides. The iodides consequently yield the largest crystals while the chlorides give the smallest.

Methods of Analysis.—The products were carefully examined, and nothing was analyzed that was not homogeneous. The crystals, which, in several instances, were large and fine and in no case hygroscopic, were freed from mother liquor with great care by pressing and crushing them on smooth filter-paper. They were then simply air-dried for analysis.

Cadmium was precipitated as sulphide, this was dissolved in hydrochloric acid containing bromine, and after the free acid had been removed by evaporation, the cadmium was precipitated with potassium carbonate solution and cadmium oxide was weighed on a Gooch filter. The cæsium in the filtrate from the cadmium sulphide was determined as normal sulphate. The halogens were determined in separate portions by the usual gravimetric method.

In every case, at least two separate crops of a salt were made and analyzed, so as to avoid any chance of mistakes arising from mixtures.

2:1 Casium-Cadmium Chloride,  $Cs_2CdCl_4$ .—This salt is produced as a precipitate when a solution of cadmium chloride is added to a concentrated cæsium chloride solution. The precipitate dissolves upon warming the liquid, and crystallizes out in very small, rectangular plates when the solution is cooled. Its formation was observed when  $50^{g}$  of cæsium chloride and  $3^{g}$  of cadmium chloride were used, and it continued to be produced with the same amount of cæsium chloride until the amount of cadmium chloride had been increased to  $18^{g}$ , at which point the 1:1 salt began to form. The salt is very sparingly soluble in cæsium chloride solutions

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and it is probably due to this fact that no chloride of the 3:1 type could be obtained.

Three separate crops gave the following results on analysis :

	Found.		Calculated for $Cs_2CdCl_4$ .
Cæsium 51	·55 51·26	51.51	51.35
Cadmium 21	.45 21.50		21.62
Chlorine 27	03 27.14	26.90	27.03
100	0.03 99.90		100.00

1:1 Casium-Cadmium Chloride, CsCdCl<sub>s</sub>. — This was obtained only as a white crystalline powder. It is formed under a very wide range of conditions, being produced by the recrystallization of the preceding salt, and continuing to appear until the solution is saturated with cadmium chloride. It is very difficultly soluble, especially in concentrated cadmium chloride solutions, and it can be recrystallized unaltered from water. Two samples, obtained under widely different conditions, were analyzed.

	For	and.	Calculated for CsCdCl <sub>3</sub> .
Cæsium	38.11	37.60	37.84
Cadmium	31.80	31.97	31.86
Chlorine	30.17	30.25	30.30
	100.08	99.82	100.00

3:1 Cæsium-Cadmium Bromide,  $Cs_sCdBr_s$ . — This compound was obtained in the form of rectangular plates, sometimes as much as  $10^{\text{mm}}$  in diameter. It can be made from a solution of  $80^{\text{g}}$  of cæsium bromide and  $4.5^{\text{g}}$  of cadmium bromide in sufficient water to make a volume of  $120^{\text{cc}}$ . On recrystallization it gives CsCdBr<sub>s</sub>.

Two separate samples were analyzed.

	Found.		Calculated for Cs <sub>3</sub> CdBr <sub>5</sub> .
Cæsium	44.25	44.27	43.80
Cadmium	11.88		12.29
Bromine	43.79	43.77	43.91
	99.92	,	100.00

2:1 Cæsium-Cadmium Bromide, Cs<sub>2</sub>CdBr<sub>4</sub>.—This was obtained in the form of slender needles, usually colorless, but sometimes possessing a pale violet color for some unknown reason. A solution  $120^{\circ\circ}$  in volume, containing  $3^{\circ}$  of cadmium bromide and  $52^{\circ}$  of cæsium bromide gave this salt. When recrystallized from water, it gives, like the preceding salt, the compound CsCdBr<sub>2</sub>. The following analyses of separate crops were made. No. IV was a simple of the pale violet variety.

I.	Found II.	d. III.	IV.	Calculated for $Cs_2CdBr_4$ .
Cs 40.46	40.53		40.46	38.11
Cd 14.55	14.62	14.68	14.78	16.02
Br 45.12	44.97	45.04	45.04	45.84
100.13	100.12		100.28	100.00

Although the analyses agree well among themselves, it is noticeable that they vary considerably from the calculated composition. This disagreement is probably due to contamination with cæsium chloride, resulting from the large surface exposed by the slender crystals and the concentration of the motherliquor. Moreover, analogy with the chloride and iodide makes the simple formula  $Cs_2CdBr_4$  far more probable than the complicated formula  $Cs_7Cd_3Br_{13}$  with which the analyses correspond.

1:1 Casium-Cadmium Bromide,  $CsCdBr_s$ .—The conditions under which this compound is formed are very wide in range, for it is produced by recrystallizing  $Cs_sCdBr_s$  and it continues to appear as cadmium bromide is added until the solution is saturated with this very soluble salt.

The compound is evidently dimorphous. One form occurs as a crystalline precipitate, apparently isometric in form, under narrow limits of conditions when cæsium bromide is in excess, being produced when Cs<sub>2</sub>CdBr<sub>5</sub> is recrystallized from water. The other form occurs in well crystallized prisms, and is obtained when Cs<sub>2</sub>CdBr<sub>4</sub> is recrystallized and when cadmium bromide is in excess of this proportion. It is interesting to notice that we have described a cæsium-lead bromide\* of this type, CsPbBr<sub>3</sub>, which is dimorphous, and that one of us has described the dimorphous mercuric compounds,<sup>+</sup> CsHgCl, and CsHgBr<sub>3</sub>, which also belong to the same type.

Below are the analyses of four separate samples. Number IV is the granular, isometric salt, the others represent the prismatic compound.

	I.	Four II.	od. III.	IV.	Calculated for CsCdBr <sub>a</sub> .
Cs	27.67	27.48		27.95	27.42
Cd	22.97	23.08	22.87	<b>2</b> 2 <b>·</b> 92	23.09
Br	49.49	49.42	49.33	49.30	49.49
	100.13	99.98		100.17	100.00

\*This Journal, xlv, 128. † Ibid., xliv, 225 and 228.

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#### 430 Wells and Walden—Double Chlorides, Bromides, etc.

3:1 Cæsium-Cadmium Iodide, Cs<sub>3</sub>CdI<sub>5</sub>.—This salt crystallizes beautifully in large, stout, twinned prisms which show a variety of habits. Some of the crystals obtained were as much as 50<sup>mm</sup> in diameter. Its formation was observed when 182<sup>g</sup> of cæsium iodide and 65<sup>g</sup> of cadmium iodide were dissolved in sufficient water to make a volume of 200<sup>cc</sup>.

Four crops gave the following results on analysis:

	Found.				Calculated for Cs <sub>3</sub> CdI <sub>5</sub> .
Cs	34.85	34.89	34.78		34.82
Cd	9.78	9.79	9.84	9.55	9.77
I	55.23	55.35	55.32	55.36	55.41
	99.86	100.03	99.94		100.00

2:1 Casium-Cadmium Iodide.  $Cs_2CdI_4$ . — This, like the corresponding mercuric salt, crystallizes in nearly square plates, in prisms and in intermediate forms. Some of the plates obtained were 50 or 75<sup>mm</sup> in diameter. It can be prepared by recrystallizing  $Cs_3CdI_4$  from water, and as the proportion of cadmium iodide is increased, it continues to form until the ratio of cadmium to cæsium has almost reached 1:1. The range of its formation is, therefore, much greater than that of the corresponding chloride and bromide, and it also differs from these in being recrystallizable from water. Three different samples were analyzed.

		Found.		Calculated for Cs <sub>3</sub> CdI <sub>4</sub> .
Cæsium	29.85	30.29	30.23	30.03
Cadmium	12.56	12.53	12.46	12.64
Iodine		57.27	57.42	57.33
		100.09	100.11	100.00

1:1 Cæsium-Cadmium Iodide,  $CsCdI_s$ .  $H_sO$ . — This salt forms thin plates, often 20 to  $30^{\text{mm}}$  in diameter. It is the only hydrous cæsium-cadmium halide that we have obtained, and it is stable when exposed to the air at ordinary temperatures.

It was considered doubtful whether the corresponding cæsium mercuric iodide\* contained a molecule of feebly combined water or not, but since both the cadmium and mercuric salts crystallize in thin plates, it is now believed, from analogy, that the mercuric compound was really hydrous.

The compound under consideration is formed under wide limits of conditions when the cadmium present is atomically equivalent to or in excess of the cæsium. It can be recrystallized from water. The samples analyzed were prepared under widely varying conditions.

\* This Journal, xliv, 230.

		Found.	Calc	ulated for CsCdI <sub>3</sub> .H <sub>2</sub> O.	
Cæsium	20.89	20.75		20.66	
Cadmium	17.13	17.43	17.89	17.39	
Iodine	59.21	59.18		59.16	
Water	2.88	2.80	2.76	2.79	
	100.11	100.16		100.00	

Sheffield Scientific School,

New Haven, Conn., August, 1893.

ART. LVIII.—On the Double Chlorides, Bromides and Iodides of Casium and Zinc, and of Casium and Magnesium; by H. L. WELLS and G. F. CAMPBELL.

THE cæsium-mercuric and the cæsium-cadmium halides have already been studied in this laboratory, and it has seemed desirable to extend the investigation to the zinc and magnesium compounds, thus completing the study of the cæsium double halides of this family of bivalent metals as far as the chlorides, bromides and iodides are concerned.

We have obtained the following salts :

3:1 Type.	2:1 Type.	1:1 Type.
Cs <sub>s</sub> ZnCl <sub>5</sub>	Cs <sub>2</sub> ZnCl <sub>4</sub>	?
Cs <sub>3</sub> ZnBr <sub>5</sub>	Cs <sub>2</sub> ZnBr <sub>4</sub>	?
Cs <sub>3</sub> ZnI <sub>5</sub>	$Cs_2ZnI_4$	?
		$\mathrm{CsMgCl}_{3}.6\mathrm{H}_{2}\mathrm{O}$
		$CsMgBr_{3}.6H_{2}O$
	-,	

A systematic and thorough search has been made in all cases, and it is remarkable that while mercury gave six types of cæsium double salts and cadmium gave three, only two could be obtained with zinc and one with magnesium. It is evident that the variety of these double salts increases with the atomic weight of the bivalent metal. The existence of zinc salts of the 1:1 type is suspected, but the suspected products were obtained only in extremely concentrated zinc halide solutions of such a syrupy nature that no satisfactory analyses of them could be made.

The previously described double halides of zinc and magnesium with the alkali-metals, as far as we have been able to find them, are given below:

3:1 Type.	2:1 Type.	1:1 Type.
(NH <sub>4</sub> ),ZnCl <sub>5</sub>	$(\mathrm{NH}_{4})_{2}\mathrm{ZnCl}_{4}$	NH ZnCl . 2H O
<b>1 1 1 1</b>	$(\mathrm{NH}_{4})^{*}_{2}\mathrm{ZnCl}_{4}^{*}$ . H <sub>2</sub> O	KZnI,
	Na,ZnCl, . 3H,O	NaZnI <sub>3</sub> .1½H <sub>2</sub> O
	K <sub>2</sub> ŽnCl <sub>4</sub>	NaZnF,
	$(\dot{N}H_4)_2 \ddot{Z}nBr_4$	KZnF,
	$(\mathrm{NH}_{4})_{2}\mathrm{ZnI}_{4}$	NH <sub>4</sub> MgCl <sub>2</sub> . 6H <sub>2</sub> O
	Na,ZnI, . 3H,O	NaMgCl <sub>3</sub> .H <sub>2</sub> O <sup>*</sup>
	K <sub>2</sub> ŽnI <sub>4</sub>	KMgCl, 6H,O
	$\mathbf{K}_{2}^{T}\mathbf{Z}\mathbf{n}\mathbf{F}_{4}$	RbMgCl, . 6H,O
	$(\dot{N}H_4)_2 ZnF_4 \cdot 2H_2O$	NH4MgBr3.6H2O
		KMgBr, 6H,O
		$\mathrm{NH}_{4}\mathrm{MgI}_{3}$ . 6 $\mathrm{H}_{2}\mathrm{O}$
		KMgI, 6H <sub>2</sub> O
		NaMgF <sub>3</sub>

There is but a single 3:1 salt, corresponding to our new cæsium compounds of that type. This was described by Marignac. A few 1:1 zinc salts have been described, hence it is remarkable that cæsium zinc salts of this type could not be obtained in a pure condition, for previous experience in this laboratory has shown that cæsium usually forms less soluble and more stable double halides than the other alkali-metals. All the previously described magnesium salts belong to the 1:1 type\* to which our cæsium salts belong, and like the latter nearly all have six molecules of water.

The cæsium-magnesium bromide is formed under narrower limits of conditions than the chloride, while no iodide could be prepared, for cæsium iodide crystallized unchanged from syrupy solutions of magnesium iodide. This behavior was quite unexpected in view of the fact that the ammonium and potassium double iodides are known, and we have here another instance where cæsium, in spite of its usual tendency to form double salts, is inferior in this respect to other alkali-metals. The idea suggests itself that great differences between the atomic weights of the alkali-metal and the less positive metal are unfavorable for the formation of double salts, but more facts will be necessary in order to establish such a rule.

The cæsium-magnesium salts show an increase in ease of formation from the iodide to the chloride. Such a gradation, both in variety of salts and ease of preparation, is evident in a number of series of double halides which have been studied in this laboratory, and the well known tendency of fluorides to form double salts indicates that the gradation probably extends to these compounds.

\*Lerch has shown (J. Pr. Ch., II, xxviii, 338) that the salts 2KBr. $MgBr_2$ . $6H_2O$  and  $2NH_4Br$ . $MgBr_2$ . $6H_2O$  of Löwig do not exist.

3: 1 Casium-Zinc Chloride, Bromide and Iodide, Cs.ZnCl., Cs, Zn Br, and Cs, Zn I, -- Each of these salts crystallizes in colorless prisms, apparently monoclinic in form. They are produced by making aqueous solutions of the constituents in the calculated proportions, but in the case of the iodide, with these proportions the 2:1 salt may form if the solution is too dilute. The salts under consideration continue to form as the relative amounts of cæsium halides are increased until the latter crystallize upon them. This indicates that no double salts with a higher proportion of cæsium exist. The iodide forms under rather wider limits of conditions than the other two salts and it usually forms larger crystals. All the salts require concentrated cæsium halide solutions for their preparation, and the chloride especially is difficult to obtain in sufficient quantity for analysis unless as much as one or two hundred grams of the cæsium halide is used. The following analyses were made, all of which represent separate crops.

				Calculated for
	_	Found.		$Cs_{3}ZnCl_{5}$ .
Cæsium	62.46			62.20
Zine	10.08	9.	80	10.13
Chlorine	27.43	27.	34	27.67
		Found.		Calculated for Cs <sub>3</sub> ZnBr <sub>5</sub> ,
Cæsium	47.12			46.18
Zinc	$7 \ 32$	7.54	7.87	7.52
Bromine	45.91	46.54	45.85	46.30
		Found.		Calculated for Cs <sub>3</sub> ZnI <sub>5</sub> .
Cæsium	36.54	36.20	36.08	36.30
Zinc	5.77	5.95	5.74	5.92
Iodine	56.89	57.16		57.78

2:1 Cæsium-Zinc Chloride, Bromide and Iodide,  $Cs_2ZnCl_4$ ,  $Cs_2ZnBr_4$  and  $Cs_2ZnI_4$ .—These salts form colorless plates, decreasing in size from the iodide to the chloride. They are all readily produced when larger proportions of the zinc halides are used than are necessary for the 3:1 compounds and they recrystallize from water unchanged. They continue to form, through a wide range of conditions, as more of the zinc halides are added until the solutions become syrupy. In extremely syrupy solutions crystals of a different appearance were noticed, but on account of the nature of these solutions, no satisfactory analyses of these products could be made. It seems probable that they were 1:1 salts, analogous to the cadmium salts of that type.

The following analyses of separate crops were made:

•	Fo	und.	$\begin{array}{c} \operatorname{Calculated} \operatorname{for} \\ \operatorname{Cs}_2 \operatorname{ZnCl}_4. \end{array}$
Cæsium	55.97	56.09	56.26
Zine	13.49	13.87	13.72
Chlorine	29.89	29.97	30.02
	F	ound.	Calculated for $Cs_2 ZnBr_4$ .
Cæsium	40.68		40.86
Zine	9.53	9.72	9.98
Bromine		49.17	49.16
1	F	ound.	Calculated for $Cs_2ZnI_4$ .
Cæsium	31.49	31.55	31.70
Zinc	7.61	7.82	7.75
Iodine	60.43		60.55

Cæsium-Magnesium Chloride and Bromide,  $CsMgCl_s.6H_sO$ and  $CsMgBr_s.6H_sO$ .—These salts form colorless, rectangular plates or flat prisms which are often striated. A thorough search gave no indications of salts of other types. The chloride is formed under a wide range of conditions, the bromide under a much narrower range while no double iodide at all could be prepared.

The following analyses were made of separate products:

	Found.		Calculated for $CsMgCl_3 \cdot 6H_2O$ .
Cs 37.14	35.60	3	35.77
Mg 6.80		. 6.83	6.23
Cl 29.84	30.13 29.70	29.55	28.65
Н_0	30.93		29.05
	Found.		Calculated for CsMgBr <sub>3</sub> . 6H <sub>2</sub> O.
Cs 27·23	27.67		26.32
Mg 4·96	4.50	5.07	4.81
Br 48.93	48.65		47.51
H <sub>2</sub> O 18.32		22.33	21.37

It should be mentioned that Dr. H. L. Wheeler of this laboratory has attempted to prepare a double chloride of cæsium and beryllium. He found that the simple salts crystallized side by side from sufficiently concentrated solutions, and there were no indications of the existence of any double salt, even at rather low temperatures. It is therefore evident that beryllium follows the rule, already indicated, that in this family of bivalent elements, Be, Mg, Zn, Cd, Hg, the tendency to form double halogen salts increases with their atomic weights.

Sheffield Scientific School. New Haven, Conn., August, 1893. A. F. Foerste-Fossil localities in the early Paleozoics. 435

# ART. LIX.—New fossil localities in the early Paleozoics of Pennsylvania, New Jersey and Vermont, with remarks on the close similarity of the lithologic features of these Paleozoics; by AUG. F. FOERSTE.

# [Published by permission of G. K. Gilbert, Chief Geologist U. S. Geological Survey.]

THE general distribution and succession of the paleozoic rocks of New Jersey, east of the Kittatinny Mountains and west of the Green Pond Mountain ranges and of the more southern part of the Triassic area, were clearly understood by the former State geologist George H. Cook and his assistants, at an early date. The folding to which this territory had been subjected was too simple, structurally, not to be easily unravelled. Immediately below a great conglomerate series on the eastern side of the Kittatinny Mountains, now known as the Oneida conglomerate, lay a great mass of sandy shales, or slates, constituting the Hudson River shale horizon. Below this was a great thickness of limestones, generally whitish in color, from which fossils were known at an horizon, lithologically somewhat distinct. This horizon consisted of a bluish, at times dark blue limestone, at the very top of the limestone group, just underneath the shales, and almost always contained To find fossils at this horizon it is only necessary to fossils. follow the trend of the formation and to keep a sharp lookout. The fossils are often small, but were early identified as The white, often magnesian, limestones beneath, Trenton. composing almost all of the limestone series were clearly separable from the Trenton horizon, as a Magnesian series. No fossils were found and so their age was properly left a little indefinite, except as regards their pre-Trenton character. Beneath the limestones, a sandstone belt of moderate thickness was known to be almost universally present. As sandstones at the base of the paleozoic series were then understood, it was possible to interpret this basal sandstone only as Potsdam, a lithological interpretation, which since has lost its value. Beneath this sandstone occurred crystalline rocks, white limestone, gneisses, massive granites, and dykes, but except in northern Sussex county, no igneous rocks were known to penetrate the paleozoic series, and even there such penetration was limited to certain dike rocks, with limited contact metamorphism. These rocks were called Archæan. Some who are at present working in this field suspect that a part of these rocks will have to be eventually classed as Algonkian but that is a new

discrimination, and was one not to be expected of the older survey.

The work of the older New Jersey survey will therefore practically stand. It is a matter of regret that on the later published geological maps, the Trenton horizon and the socalled Potsdam were not designated by separate colors. But the survey was eminently an economical one, and these horizons representing narrow outcrops of no practical value, and being universally present, where surface deposits did not obscure the geology, and their outcrops being parallel to the upper and lower limits of the limestone series, they offered no inducement to separate mapping on a map with the small scale of five miles to the inch; moreover the expense of printing would have been greatly increased. The more recent discoveries in this region are therefore not so radically new as at first sight might appear to be the case, but they are important from the point of view of paleontologic stratigraphy. They did not change the stratigraphy but they affected the terminology of the lower of the beds here considered.

While Mr. Nason was studying the White Limestone region of Sussex County, New Jersey, he had the assistance of Dr. C. E. Beecher in the paleontological part of the work. Dr. Beecher found trilobites-Olenellus-in the sandstone at Hardistonville (with Scolithus) (5) and also in the sandstone about a mile south of here at a point near locality 7 on the accompanying map, and Mr. Nason himself, found a fragment of a trilobite, presumably Olenellus, near Franklin Furnace, but in his section XIV the exact locality is not indicated. Dr. Beecher also found a species of Obolella in what are very probably the lower parts of the Magnesian limestone series in the old furnace quarry north of the western half of Franklin Furnace Pond; and fossils were also found by him in "the unchanged blue limestone" (Nason) stratigraphically above the Olenellus sandstone at Hardistonville.\*

As a result of these observations the basal part of the Magnesian limestones (and also the white limestone according to Mr. Nason's views of correlation) and the sandstone here formerly called Potsdam were ascribed to the Olenellus horizon.

Mr. Nason was especially engaged in the study of the white limestones. Consequently he did not follow up the outcrops of the Olenellus sandstone very closely, as is indicated by various omissions within the range of his published map, and by the outlining of various sandstone outcrops. He did not

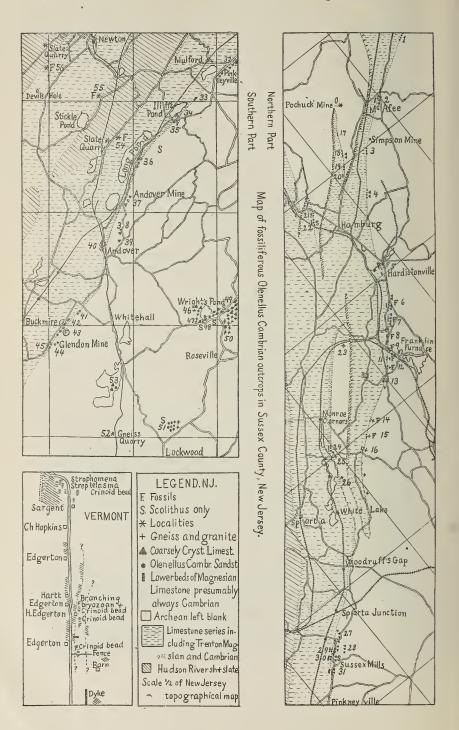
<sup>\*</sup> Ann. Rep. of State Geol. of New Jersey, 1890—The Post-Archæan Age of the White Limestones of Sussex County, N. J., by Frank L. Nason, pp. 31, 43, 55, 46, 49, sections X, XIII, XIV.

work his way far enough out of the metamorphic white limestone region to see that his discoveries necessitated the relegation of all the so-called Potsdam sandstones and basal Magnesian limestones and these alone to the Olenellus horizon. This is shown by his final conclusions that a careful search for fossils must be made "in the whole belt, or rather belts of limestones, sandstones, slates, and shales hitherto called and regarded as Potsdam, *Trenton*, and *Hudson River*" (italics not in the original. See pages 49, 50 of the Report.)

When the writer was called into New Jersey by the needs of the survey of the Archæan Highlands under the more immediate charge of Prof. J. E. Wolff and his assistant, Mr. R. S. Tarr, his first duty was to trace the Cambrian sufficiently out of the metamorphic area to determine what was Pre-Cambrian and the second was to investigate the doubts recently thrown upon the previous determinations of Trenton and Hudson River strata.

The last was quickly solved by an irregular section from the Archæan at Andover to the Oneida conglomerate of the Kittatinny Mountain range at Culver's Gap. The thin blue limestone overlying the Magnesian limestones and underlying the Hudson River was found to everywhere contain fossils, such as are found in Trenton rocks. In the thin blue limestones of this section fossils were for instance found on the eastern side of the road running north about half a mile west of Long Pond, and some distance north of an old slate quarry, on the eastern side of a synclinal (54). Also on the western side of this synclinal, directly west of a strong bend in the road almost half a mile north of Stickle Pond (55). Again on the eastern side of the next synclinal, three-eighths of a mile directly south of the great slate quarries a short distance southwest of Newton (56). This exposure is in a field, on the eastern slope of the hills. Also on the western side of this second synclinal, along the New York, Susquehanna & Western railroad track a short distance south of Augusta, at a curve in the railroad. Finally, half a mile east-northeast of Branchville, where this limestone finally disappears under the Hudson River, so as not to appear again in western New Jersey.

Parts of the first task were equally easy owing to the simplicity of the strike and dip of the Olenellus sandstone which varies too little from outcrop to outcrop to make it difficult to trace the formation. Moreover in most of the outcrops in the fairly continuous line of exposures between Hardistonville (5) and the locality two miles southwest of Franklin Furnace (15), fossils are very abundant in certain layers of the sandstone, so that they are very readily found. Their locations are sufficiently indicated in the accompanying map. Fossils are



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again found at various points along the line of outcrops extending from the road corner south of Sparta Junction (29) to a point about half way between Andover and Tranquility (45). These exposures are also sufficiently well located on the accompanying map. But along this second line, fossils, except Scolithus, are rare, and the decisive locality is the one carrying Olenellus and other fossils at the strong bend in the road southeast of Iliff's Pond, as the pond northeast of Long Pond is called (35). At the various localities examined Olenellus was found at 5, 6, 7, 8, 9, 11, 12, 14, 15, and 35. A trilobitic fragment resembling Ptychoparia was found at 43. Species of Hyolithes were also seen, one resembling H. Americanus, at 11, and another resembling H. communis, at Various forms of the burrowed tubes known as Scolithus 14. were very common at many localities; they were found at 5, 8, 9, 11, 14, 15, 22 (rare), 30, 35 on the hillside between 35 and 36, 51, and in the reddish siliceous limestones, weathering at times to shale, and in the intercalated sandstones at 48, 49, and 50.

Any one at all closely observant will notice at once that even in this limited area the Scolithus burrows were not all made by the same species of animal. In the fine grained siliceous limestones near Wright's Pond, 48, 49, 50, the burrows are narrower, usually 2<sup>mm</sup> in diameter or less, and closer together and reach a length of 60<sup>mm</sup>, or more, and they are nearly straight and vertical to the bedding. This form is also found in rocks of similar lithological character in some of the exposures between Andover and Hardistonville. It was evidently a somewhat more gregarious species than the ordinary form, and preferred muddy bottoms while the ordinary form chose a sandy habitus. A second form resembles the ordinary type in choosing a sandy bottom. It had perhaps slightly larger burrows, about 3<sup>mm</sup> in diameter, or at times a little larger. Its chief distinction lies however in its burrowing habit, which was not distinctly vertical but the burrows are irregular in direction, as though the animal after having entered the sandy bottom, extended its burrows in a more or less irregularly horizontal direction. It may represent a totally different class of animals from those of the vertically burrowing forms. It has been seen only at 51, near Lockwood, but there it is abundant.

Lithologically the Olenellus Cambrian sandstone can be traced into eastern Pennsylvania, its limited thickness and constant characters throughout this extent with the knowledge that the base of the Magnesian limestone series in New Jersey at least is Cambrian, making it probable that all hitherto called Potsdam in eastern Pennsylvania is now to be classed as Olenellus Cambrian until fossils are found which will shed further light on the subject. That the lower paleozoic section of northern New Jersey is still preserved in all its features in eastern Pennsylvania is readily seen along the magnificent sections offered by the Lehigh between the Kittatinny range and Bethlehem. Underlying the Oneida conglomerate of Kittatinny Mountain, are the shales and slates of the Hudson River series. The top of the underlying great limestone series is again an especially constant fossiliferous horizon of Trenton age. As in the Vermont localities to be described later, these Trenton fossils occur not only at the top of the limestone series, but also in thin beds of limestone intercalated in the base of the shales referred to as Hudson River. Such intercalated limestones containing Trinucleus and other fossils may be seen toward the base of the shales on the road leading diagonally from North White Hall P. O. on the railroad, southward up hill above the cement works along the track,  $2\frac{1}{2}$ miles north of Hockendauqua. Below the limestone series the basal Cambrian sandstone occurs again, of moderate thickness, having here however the character of a quartile, there being no disintegration, as in most of the New Jersey exposures. The base of the sandstone is distinctly conglomeratic, and rests unconformably upon Archæan gneisses, but with a less marked angle of discordance than in the northern New Jersey exposures. Some of the lower beds of sandstone are tinged with purple, and in these it is not uncommon to find large coarse tubes, burrowed vertically into the sand, varying from 10 to 20<sup>mm</sup> in thickness and from 70 to 150<sup>mm</sup> in length, usually filled up with a lighter colored sand than the rock in which they are found, being evidently the same kind of sand as that forming the next higher layer, in each case. The wash of the sea seems to have partly broken down the top margin of the tubes before the filling with sand was completed, the result is a tube of the appearance of Monocraterion Lesleyi Prime, found in the basal members of the limestone series, a quarter of a mile northwest of Helfrich's Spring and again in limestone three quarters of a mile northwest of Durham iron works. Although this is a tempting opportunity to conclude that these tube casts indicate the Cambrian character of the basal portions of the limestone series, a fact already known for New Jersey and Vermont, it must be admitted that worm burrows are hardly to be given the value of determinative fossils.

While the New Jersey Survey has always acknowledged the Green Pond Mountain series as a *terra incognita* or at least a region of many unsettled questions, as is evidenced among other things by the coloring it was obliged to employ in its

geological maps, it had nevertheless in later years laid the basis for its solution. East of Newfoundland in the back lots of some of the last houses, on the southeast side of the hill, fairly good and abundant Oriskany fossils had been found in situ. A mile and a half south of Newfoundland, where the road crosses the stream, the valley contains at various places large bowlders with Helderberg fossils, suggesting that the northeast, southwest valley here was filled in part by this series. Since the rocks all dip west the coarse conglomerates forming the eastern side of Copperas and Kanouse Mountains must be Oneida, the red sandstone above the same the Medina, the underlying limestone, the Magnesian limestone, and the basal sandstone, Cambrian, but instead of the term Potsdam, it is necessary now, until further development to call it Olenellus Cambrian. It is a quartzitic sandstone, from 10 to 15 feet thick and so far has not furnished fossils. The unconformity indicated by the absence of the Hudson River shales east of Kanouse Mountain, and its increased emphasis southwards, by the additional absence of the Magnesian limestones and the Olenellus Cambrian sandstone, are facts already appreciated at the time of the publication of the Final Report of 1868. That part of the lower paleozoic section which is exposed here, agrees with what has been found farther west, in the area between the Archæan areas and the Kittatinny Mountains.

With these sections as exhibited in New Jersey and eastern Pennsylvania, the Vermont lower paleozoic rocks show a striking similarity. That the sandstones along the western flanks of the Green Mountain area were Olenellus Cambrian was made sufficiently evident by the work of Mr. C. D. Walcott (The Taconic System of Emmons, and the use of the name Taconic in geologic literature.) The Stockbridge limestone of Vermont corresponds to the Magnesian limestone of New Jersey. At its top there is again a thin blue or dark blue limestone bed, occasionally recurring, as in Pennsylvania, as thin beds intercalated in the basal portions of the overlying shales, and containing a Trenton fauna. As in New Jersey, localities for fossils can be multiplied in this horizon almost ad libitum. Localities discovered by the writer are mentioned in the publication of Prof. J. E. Wolff (On the Lower Cambrian age of the Stockbridge limestones at Rutland, Vermont, Bull. Geol. Soc. America, vol. ii, 1891), and of Mr. T. N. Dale (On Plicated Cleavage-Filtration, this Journal, vol. xliii, p. 317). But these are only a part of the localities found and none of the more southern ones are given. A few are here appended, the most southern being near Danby Four Corners, making thus a length of twelve miles from

Rutland southwards, in which this thin blue Trenton limestone, usually not exceeding thirty feet in thickness and often much less, is known to occur. At Danby Four Corners one exposure lies about two miles southwest of the town in the fields near woods; a second is seen directly northeast of the corners in the southwestern part of a large open field. Taking the road leading west of South Wallingford to its junction with the west valley road, which follows the eastern side of the long range of hills bounding the western side of the Rutland South Wallingford Valley, an exposure of this fossiliferous blue limestone can be found by going diagonally up the hill, in a general northwest direction, to a sort of open bench above a more steeply inclined wooded line on the hillside, a considerable distance from the road. Passing from the same junction of the roads northward, a series of exposures are found along the eastern flank of the hill range. Their location is sufficiently shown by the accompanying hasty sketch The fossils are few in number, and the geology is commap. plicated by strike faults, and would not be readily understood had the geology not been unravelled by Prof. J. E. Wolff and Mr. T. N. Dale, farther north where it is less complicated. The most interesting locality is that northwest of Sargent's house some distance south of the bend of the road, where the rock shows cross sections of Streptelasma and Strophomena.

Above this Trenton limestone especially west of West Rutland Valley, occurs a great series of shales and sandstones of Hudson River ages, while the coarse conglomerates of Bird Mountain seem to correspond to the Oneida of New Jersey and eastern Pennsylvania sections.

While Dr. Beecher was discovering Cambrian fossils in the basal portions of the Magnesian limestone series in northern New Jersey, the writer, in the summer of 1890, was also finding Cambrian fossils at various points in the Stockbridge limestone north of Rutland, which he also was inclined to view as of Olenellus Cambrian age. Later Prof. Wolff added to these localities. The following year Mr. T. N. Dale found others in the limestones of Center Rutland Valley, west of Clarendon, and the writer later in this second year also collected here, discovering that the Cambrian fossils-chiefly Hyolithesoccurred in a bed having a long strike exposure, and finding a few fossils also below this bed. While these fossils no doubt belong to the lower portions of the great Stockbridge limestone series, yet it is probable that this Cambrian portion extends a considerable distance up into the series, although how far is as yet unknown. At present the writer is more inclined to consider these fossils as very high up in the Olenellus Cambrian, or forming a transition to the Middle Cambrian, but the

fauna is still too meager. The horizon corresponds evidently to the Cambrian portion of the Magnesian beds in New Jersey.

While fossils are not common in the upper or middle portions of the Magnesian limestones in eastern Pennsylvania and New Jersey, or of the Stockbridge limestone in the southern half of Vermont, still they are found. In the publications of the Pennsylvania Geological Survey such localities are mentioned and they occur also in the West Rutland valley both northeast and southwest of the town. The fossils are such as to make evident their Lower Silurian character. They are found beneath the thin dark blue Trenton limestone. So their general reference to the Chazy-Calciferous is warranted (J. D. Dana, An account of the discoveries in Vermont geology of the Rev. Augustus Wing, this Journal, 1877). The basal portions of the Hudson River formation at West Rutland and elsewhere in southern Vermont is often represented by dark, black shales of that peculiar lithological character which at once suggests the presence of graptolites but these have so far not been discovered. In New Jersey, however, the writer is informed by Prof. J. C. Smock, the State Geologist, that graptolites were found by Dr. C. E. Beecher along the railroad track between Pattenburg and Midvale. Near Hoosick, New York, graptolites occur at the same horizon (C. D. Walcott, The Taconic System of Emmons). They will probably be found some time in Vermont.

The chief difference between the lower paleozoic sections in the southern half of Vermont between the Taconic and Green Mountain areas, and those of New Jersey and Pennsylvania lie in the fact that in Vermont the typical Olenellus sandstone, besides being thicker, overlies a considerable thickness of other sandstones, and conglomerates, evidently belonging to the same geological unit, but of which, in the absence of fossils, the precise age cannot be definitely determined. In other respects the correspondence is striking, necessitating the belief that both regions have passed through a closely similar geologic history, and as such might be said to belong to the same geologic province, that Atlantic province extending of course much farther south than eastern Pennsylvania. This similarity is the more striking owing to the dissimilarity from this simplicity of lithologic structure in regions farther north and west and southwest than the various Rutland Valley belts of southern Vermont, as here discussed. This can be partly accounted for by the fact that the Adirondacks in earlier paleozoic times formed a separate source of sediments, and surrounded themselves by a series of rocks whose lithological characteristics are somewhat at variance with those deposited at a greater distance. The sphere of their influence extended into northwestern Vermont,

and for a considerable distance southwards in western Vermont and eastern New York. It is probably in part for this reason that the geology of Rensselaer and Washington Counties is so difficult to unravel and no longer presents the same simplicity of lithologic structure found east of the Taconic range. Lithologically this difference consists in the introduction of argillaceous and sandy limestone, shale and sandstone elements into that part of the early paleozoic scale which is represented in New Jersey and southward by the Magnesian limestone, and in the southern half of Vermont by the Stockbridge limestone, in other words that part of the section between the Hudson River (including for the present the Trenton limestone in the great limestone series) and the top of the Olenellus Cambrian sandstones. How far southward the sphere of influence of the Adirondack sedimentation extended, is unknown. To what extent, the Archæan of the Highland region between Newburgh and Peekskill supplied sediments to the early paleozoic series as here discussed is also still undetermined. The remarkable agreement between the southern Vermont and the New Jersey, eastern Pennsylvania, and more southern sections and the great longitudinal extent of the area having this structure would however lead to the conclusion that these sections represented the main lithologic features of eastern early paleozoic geology; a basal Cambrian sandstone, overlain by a great series of limestones embracing a considerable vertical range of faunas, and a great mass of Hudson River slates and shales and sandstones, overlain finally with more or less unconformable Oneida conglomerate, the unconformability in many places being more theoretic than evident structurally, while in others it is also strongly marked structurally, and always paleontologically. Variations from this lithological type would seem to be due more to local features, sometimes of vast influence as in the case of the Adirondacks, at other times of more limited range. To study out these more local influences as something distinct from the general, to discover their source and their range is a part of the geology of the immediate future.

The various questions of correlation here discussed are of course not new. They are here brought out again chiefly to emphasize the strong agreement between the sections of the early paleozoics in the southern half of Vermont between the Taconic and Green Mountain ranges, and those of New Jersey, eastern Pennsylvania and southwards, an agreement the more remarkable since closely contiguous areas west of the Taconic ranges, in western Vermont, and Massachusetts, and in eastern New York do not show the same simplicity of lithologic structure. ART. LX.—An apparent Time-break between the Eocene and Chattahoochee Miocene in Southwestern Georgia; by RAPHAEL PUMPELLY.

THROUGH the southwestern part of Georgia and adjacent northern Florida there extends a plateau known as the Red Clay hill region. It has a maximum altitude approximately 300 feet above the sea, and an undulating surface, with the main drainage channels cut, with steep cross profiles, to a depth of over 100 feet.

This plateau is sharply limited on the north by an often steep declivity facing the Eocene flat-land country, and consists of Miocene deposits resting on Eocene, both of which dip about 13 feet to the mile to the South. The section along the Flint River where it is cut into the flat-land country, exposes the limestone and siliceous Eocene beds abounding in Vicksburg fossils. Of these Mr. Foerste writes me, that they form "a varied fauna, including species of Operculina, Orbitoides, many corals, Cidaris, Echinocyamus, Clypeaster, Scutella, Lunulites, Ostrea, Pecten, Amusium, Spondylus, Plicatula, Cardium, Turritella, Vermetus, Xenophora, Natica, (Ampulina), Cerithium, Strombus, Cypræa, Cassidaria (Sconsia), Fulgur, Conus and fragments of claws of crabs; among these species Echinocyamus parous, Eumnus, Scutella Lyelli, Pecten Poulsoni, and unknown species of Pectunculus and Cerithuum may be mentioned as especially characteristic of the Vicksburg horizon in Southwestern Georgia."

Where the Flint River cuts through the plateau at an altitude of 40 to 50 feet above the sea, it exposes the white calcareous beds of the Chattahoochee group, but without any visible contact with the underlying Eocene. As has been shown by Mr. Langdon,\* the river bank is occupied by the Chattahoochee formation until its gentle southerly dip brings its upper surface below water, and under the Chipola Miocene group at Alum Bluff.

The base of the plateau is Chattahoochee. The exposures in sides of deep ravines and freshly eroded gullies in the plateau almost uniformly show only more or less sandy clays, which in the higher parts seem to be more sandy, and contain smooth pebbles of sandy iron-ore, which may be either clastic or concretionary, and also frequent pebbles of quartz, clearly derived from metamorphic schists. These quartz pebbles are often  $\frac{3}{4}$  to  $1\frac{1}{2}$  inches long by  $\frac{1}{2}$  inch broad, with a thickness of only  $\frac{1}{12}$  to  $\frac{1}{5}$  inch, and so angular that it is difficult to believe

\*Some Florida Miocene, this Journal, October, 1889. Variations in the Cretaceous and Tertiary Strata of Alabama, Bull. Geol. Soc. Am., vol. ii, July, 1891.

AM. JOUR. SCI.-THIRD SERIES, VOL. XLVI, NO. 276.-DEC., 1893.

that they have been transported very far. The only light obtained thus far as to the age of the upper part of the plateau is found in extensive areas of residuary fossiliferous angular fragments, representing broken-up siliceous beds. These occur at numerous points on the plateau at altitudes of 230 to 260 feet above the sea, and seem to belong below the ferruginous sand with iron ore pebbles. These fragments up to several cubic feet in size, are found covering the surface in areas of many acres in extent, and also imbedded in the underlying clays. At one locality, which we were accustomed to call Gasteropod gully, near Roseland plantation, southeast of Bainbridge, the range exposed between the fragments on the surface, and those in the clays in the adjacent gullies is as much as 60 feet or more, although under the circumstances the true relation between the upper and lower fragments is not apparent. These fragments consist of silicified beach-worn shells which either make up almost the whole rock or are imbedded in the sandstone. The fossils are of Chipola Miocene Age. Of these Mr. Foerste sends me the following list from his determinations.

"Ostrea divaricata, var., Pecten Madisonianus Arca idonea, Carditamera? protracta, Venus mercenaria, var., Strigilla flexuosa, Mactra subcuneata, Solen ensis, Conus planiceps, Drillia similar to lunata, Melongena similar to subcoronata, Typhis acuticostata, var. typhis similar to gracilis, Turritella gatunensis, Turritella with an ornamentation similar to T. acropora, but shell is larger, T.? terebriformis, Solarium bellastriatum, var. Vicksburgense, a moderate variation from the same. Crucibulum auricula var.? imbricatum, Calyptræa centralis, Crepidula fornicata, Natica floridana, Chlorostoma (Omphalius)? exoletum, Helix adamnis, var. Bulimulus? Balanus?

As stated above the surface of the plateau is generally undulating. Wherever it has been exposed to cultivation deep gullies have rapidly cut their way back into it. These facts would incline one to look upon the plateau as a Miocene island area covered and levelled up with a much more recent sand formation. The younger sands may however be of Miocene age like those above the Chipola and Ecphora beds at Alum Bluff. And they may have been continuously protected from erosion by the density of vegetation and the porosity of the rocks which permitted the downward drainage, into subterranean channels, which is still active throughout the region. This last alternative accords with the view expressed by Mr. A. F. Foerste,\* that these sands represent the shoreward extension of the Chipola and Chesapeake formations.

The evidence for a time break between the Eocene and Chattahoochee Miocene consists in :

\* Chipola Miocene of Bainbridge, Ga., and Alum Bluff, Fla. This Journal, Oct., 1893.

I. The almost general presence of a limestone conglomerate at the base of the Chattahoochee, immediately overlying Eocene fossils. This conglomerate is sometimes a breccia, and often like a rock shattered in place; but more often it consists of clearly rolled pebbles of limestone not distinguishable from the Eocene rock below.

II. The surface of demarcation between the Eocene and Chattahoochee is very irregular. The Eocene rises island-like into the Miocene. The altitude of the contact differs considerably at points but a few miles apart along the strike. Thus the contact is

180 feet above the sea on Griffin's Creek.

102 feet above the sea in Glenn's Well,  $2\frac{1}{2}$  miles eastward.

155 feet above the sea in Powell's limesink, s'ill farther east.

Mr. Foerste writes me that the fossils at Griffin's Creek correspond with those found in the upper part of the Chattahoochee, while those at Glenn's Well, and Powell's limesink correspond with those belonging in the lower half of the Chattahoochee.

At numerous points in southwestern Georgia there occur between the Eocene and Chattahoochee, masses of columnar corals chalcedonized. They are not present at the majority of the points of observed contact. Nor has their exact relation to the Eocene or Chattahoochee been observed. Mr. Dall writes me regarding some that I sent him, that they belong at the base of the Miocene. The observations lead me to think that they probably grew during the interval between the Vicksburgh and Chattahoochee, upon the submerged Eocene surface.

Mr. Alexander Agassiz, in "The three Cruises of the Blake," has called attention to the influence of submerged ridges and plateaux upon the growth of organic formations.

It seems possible that during Miocene time the present plateau of southern Georgia was outlined by submerged islands of the Eocene limestone. The Gulf Stream after the creation of the Central American barrier, found its way back to the Atlantic sweeping over southern Georgia and northern Florida, and supplying the food needed to build up the great organic beds of the Chattahoochee and Chipola.

As these grew to the surface they formed islands which would explain the presence of the land shells found in the Bainbridge Chipola, and also the beach-worn character of the Chipola fossils at the same locality. And the lower flat-land country of central Georgia may represent the contemporaneous course of the cold current, carrying less pure water, and less of the nutriment needed to build up organic deposits.

## ART. LXI.—The Rise of the Mammalia in North America; by HENRY FAIRFIELD OSBORN, Columbia College, New York.

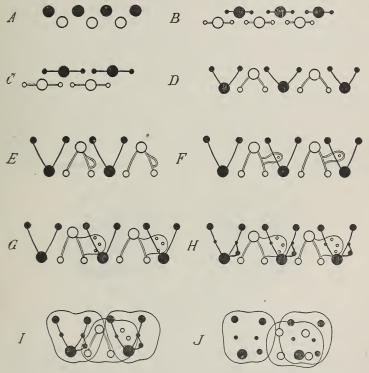
[Continued from page 392.]

#### PART II.

### Origin and Evolution of Trituberculism.

"CONCRESCENCE" is the newest theory of cusp evolutionan expansion by Kükenthal and Röse of views earlier expressed by Gaudry, Magitot and Dybowski. As Kükenthal derives three conical Cetacean teeth by splitting apart a triconodont molar, he conversely derives a triconodont molar by bringing together three reptile cones. Smith Woodward has called attention to the support the epidermal structures of the fishes give to this hypothesis, yet as applied to mammalian teeth, it comes from a one-sided Morphology which regards only the wonderful though mutilated chapters of Embryology when the untorn pages of Paleontology are at hand. Between the Trias and the Puerco, we are, so to speak, in at the birth of every successive cusp, and can observe positively that the law of cusp evolution is direct upgrowth from the smooth slopes of the crown or from the cingulum, that fertile parent of new cusps. Each new cusp is usually preceded by an abraded surface, and prophesied by an excessively minute hillock. It follows from this that cusps range in size and height directly according to their age-a principle beautifully demonstrated in some of the Mesozoic teeth. If the Kükenthal-Röse theory were correct, the oldest triconodonts should be iso-conid, whereas we know that the three equal cones of Triconodon are all a very late development; the earlier forms show the lateral cones receding to the needle-points of Dromatherium.

The tritubercular molar owes its survival to the original advantage of its triangular form, and to the possibilities of free cusp addition—as worked out by Cope, Wortman, Schlosser, Scott, and myself. Rütimeyer's term, "trigonodont," best expresses the primitive structure of the upper and lower teeth, as of two interlocking triangles with their open bases turned outward in the upper and inward in the lower jaw. These "trigons" cutting past each other, made a shear so perfect that many Insectivora retained it without further evolution. But in most Trituberculates a talon was next added to the lower molar (Jurassic stage) as a pestle crushing into the upper valley; this talon gradually widened into a broad heel supporting three cusps, as found in the Cretaceous. Consider the extreme antiquity of the three homologous cusps borne upon the back part of the human molar. This addition gave the opposed molars two shears and one crusher, and was so perfectly adapted to the needs of Lemurs and many Insectivores and Carnivores, in short, of most clawed animals, that they stopped at this point. Not so with the Herbivora, which required more extensive crushing surfaces. The upper molars, which had remained triangular through the Cretaceous and into the basal Eocene, began to develop a little talon, like that



Phyletic History of the Cusps of the Ungulate Molars. Upper molars in heavy lines, lower in light lines.

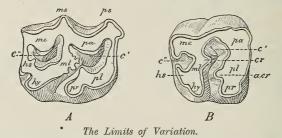
A. Reptilian Stage, Haplodont, Permian. B. Protodont Stage (Dromotherium), Triassic. C. Triconodont Stage (Amphilestes). D. Tritubercular Stage (Spalacotherium. E. Tritubercular-tuberculo Sectorial (Amphitherium).\* F. The same, in Upper Jurassic. G. The same, in Upper Cretaceous. H. The same, Puerco, Lower Focene. I. Sexitubercular-sexitubercular, Puerco. J. Sexitubercular-quadritubercular, Wahsatch.

\*Since this drawing was published I have learned that the talon of the lower molar of *Amphitherium* is considerably larger than here represented.

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early seen in the lower molars, and at the same time both upper and lower molars entirely sacrificed their primitive cutting powers, and were converted from secodont into bunodont types by bringing the primitive trigons down to the level of the talons. At the same time, the upper molars acquired intermediate tubercles, and the triangular or oblique arrange ment of the tubercles was shifted into the quadrangular or transverse arrangement. This outline is the result of fifteen years' observation.

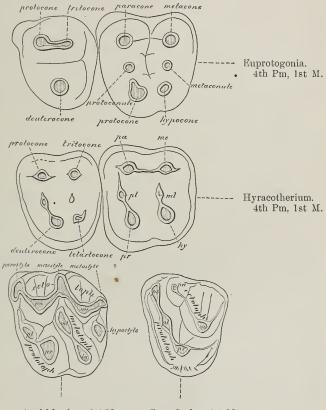
With square crowns (vs. triangular) and six conic cusps above and below the molars of the Artiodactyl and Perissodactyl Herbivora ended their first constructive period and started upon their modernization. From this point we direct our attention upon the numerous combinations of three or four forms assumed by these single cones. The important thing now is to determine at what period these combinations were established, for there is wide difference of opinion as to when ungulate divergence began. To this I refer later. Taeker has recently shown how every modern embryonic lophodont or selenodont molar first exhibits the archetypal cones of the primitive bunodont. This law, together with my own parallel studies of the evolution of the horse and rhinoceros molars, led me to the discovery that these embryonic primi-



A, Merychippus. B, Aceratherium. Showing the secondary enamel foldings of the crests arising from the centers of the ancestral cones.

tive cones are also the main growth centers, for, in the upper Miocene, long after the Perissodactyla have separated from each other, we see the influence of the archetypal form in the generic and specific variations of the molars. Compare the teeth of *Merychippus* and of *Aceratherium*, and imagine that you see underlying the diverse crests and crescents the simple bundont molar of such a form as *Hyracotherium leporinum* of the London Clay. You will then notice that the characteristic secondary folds and spurs of the Miocene teeth spring from the old bundont cones, that the two "cement lakes" of Merychippus are equivalent to the two "fossettes" of Aceratherium, because the "crescentic spurs" of the horse and the "crochet" and "antecrochet" of the rhinoceros spring alike from the primitive "intermediate tubercles."

In view of these discoveries of the uniformity of mammalian molar type, a uniform terminology has become as necessary for the dental cusps as for the carpal and tarsal elements of the feet. Professor Gaudry's once admirable system, elaborated in his "*Enchaînements*," was based upon the supposed



Anchitherium, 1st M. Coryphodon, 1st M. Homologies in the Horse and Coryphodon Molars and Premolars.

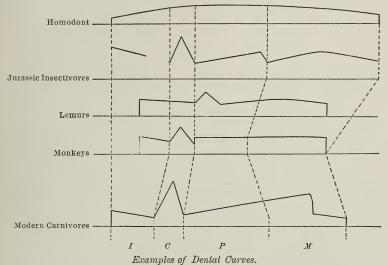
division of the ungulate molar into a "first lobe" and "second lobe," and is still followed in France. Yet it has two drawbacks: it precludes the comparison of the ungulate with the unguiculate molar, for neither lobe includes the complete triangle; still more inconvenient is the fact that we cannot compare the higher ungulates with the older Coryphodons and Periptychidæ in which the molars were developed upon the triangular plan; these teeth have only the first lobe and half the second. The upper molars of Hipparion and Coryphodon illustrate the advantages of this new system of comparison and of terminology.

Scott has made a further advance in Odontology by working out the laws of premolar evolution or cusp addition. In many groups we know that from one to four of the premolars gradually acquire the exact form of the molars in order to further increase the grinding surface, and we should a priori expect that the cusps would be added in the same order, and therefore be homologous with the molar cusps. This, as Schlosser and myself had observed, is not the case. Scott shows the order of cusp development in the premolars is very nearly the same in all the mammals, and yet is entirely different from the order followed in the molars. This law again unexpectedly ties the clawed and hoofed mammals together; the sequence of cusps in palingenesis is similar to that observed by Taeker in embryogenesis, and Scott is justified in proposing a new terminology (protocone, deuterocone, tritocone, etc.) for the premolar cusps, which will in the end prove to be a great convenience.

I alluded above to the well-known extreme and very confusing similarity of the tritubercular molars in the early stages of divergence. Trituberculism is at once the cause of clearness and of doubt when we get back to the stem mammals of widely different phyla. This has led to strange misconceptions of phyletic affinities as exemplified in Filhol's division "Pachylémuriens," a supposed mixture of lemur and ungulate stock. There was never any such mixture, and the question comes up how to distinguish unlike forms with like teeth? I have proposed to make use of a *dental curve* which will express the incipient atrophy of some parts, and hypertrophy of other parts of the series, a metatrophism which will naturally terminate in the reduction of some teeth, and excessive development of others. This has not been by any means fully worked out, but I believe it will prove to be of great service in directing attention to some of the initial tendencies of divergence, which are not expressed either in the dental formula or in the patterns of the teeth. Below are some of these curves. When worked out by the composite method, we will find certain primary curves characteristic of the ordinal divisions, and minor curves distinguishing the lesser divisions. Of course the laws of parallelism will also be found in force here; flesh-eating, insect-eating, and grass-eating animals will be apt to have similar curves even when evolved in different groups, but here the dental formula and succession will come to our aid.

### Breaks and Links in the Mesozoic Fauna.

By our hypothesis all three sub-classes flourished together during the American Mesozoic; the Marsupials disappeared, then the Monotremes, and by the end of the basal Eocene the Placentals were in exclusive possession of the northern continent.



Although we have great reason to congratulate ourselves upon the rapid progress of discovery, there still remain great gaps in Mesozoic time between certain horizons and in the lineal phyletic series of both the Mesozoic and Cenozoic. For a time standard we may take advantage of the remarkably constant evolution of the Plagiaulacidæ in the Mesozoic, and of the Equidæ in the Cenozoic—as certain invertebrates are made use of in older rocks. The grooves and tubercles of Plagiaulax and the cusps and styles of the horses are added with the precision of clockwork, and supposing that the rate of evolution has been about the same, we can approximately estimate both the periods of deposition and the intervals as below.

PLAGIAULACIDAE.

	Stonesfield.	Purbeck.	Laramic.	Puerco.	Cernaysian.
Number of Premolars,	?	4-3	2	2 - 1	1
Grooves on Premolars,	?	7 - 9	11-14	12 - 15	14
Molar Tubercles: outer; inne	r; ?	4:2	6:4	6:4	9:6

Estimating the geological intervals by dental evolution and faunal succession, there is first the great gap between the Trias of Microlestes and Dromatherium and the Jurassic of the

Stonesfield slate; there is a relatively shorter interval, but still a considerable one between this and the Purbeck or Atlantosaurus beds. Then follows another long and very important interval between the Atlantosaurus beds and the Laramie (Upper Cretaceous). The gap between the Laramie and Puerco was relatively short as indicated by the comparatively limited evolution both of the Plagiaulacids and Trituberculates. The Puerco itself was a long period in which the Plagiaulacids underwent considerable changes. Then follows an interval which it is most important to fill by future exploration, for between the Puerco and the Wahsatch the differentiation of the even and the odd-toed ungulates must have occurred. The Wahsatch proper does not mark a very extensive evolution of the forms it contains. It passes after a slight break into the base of the Bridger (Wind River) and then begins that splendid and almost uninterrupted succession of lake basins, terminating in the Pliocene. I append a table, to be compared with that published by Marsh in his admirable address of 1877, and exhibit the great progress of the last sixteen years.

The general faunal succession is marked by the sudden appearance and disappearance of certain series and rise and fall of great groups. In the Trias appears the remarkable protodont or primitive-toothed Dromatherium; we cannot determine its Order at present. We still have no American fauna corresponding to the intermediate Stonesfield of England. In the Jurassic Atlantosaurus beds the three supposed representatives of the Monotremes (multituberculates), Marsupials (triconodonts) and Placentals (trituberculates), appear in equal numbers; the latter are generally characterized by the primitive dental formula. In the Laramie the Multituberculates continue in great profusion, and the Marsupials and Placentals are also numerous.

The serial succession of the Trituberculates from the Mesozoic is still an unknown chapter; we are utterly unable to connect the Dromatheriidæ of the Trias, the Triconodontidæ, Amphitheriidæ and Amblotheriidæ of the Jura with each other, or with any Cretaceous or lower tertiary mammals. The serial relations of the Multituberculates, on the other hand, have been made much clearer by the discovery of the Laramie fauna. Cope and Marsh in this country, and Smith Woodward in England, have at last broken into the long barren Cretaceous. In studying the accurate figures published by Marsh and a large collection of teeth recently made for the American Museum by Wortman and Peterson, I find that this Laramie fauna is widely separated from the Jurassic in its general evolution, and as Gaudry, Lemoine and Cope have observed, it approaches more nearly the basal Eocene of the Puerco and

PERIODS,	HORIZONS.	CHARACTERISTIC GENERA. NEW TYPES APPEARING.	TYPES BECOMING EXTINCT.
Post or Upper	RQUUS. Dr. 2000	Equus, 5 species. Elephant, E. primigentus, Mastodon, Llanns, Camels, Eschutius, Holo- menisçus. Elk, Alces. Putugonus, Sloths, Mylodon, Guptudon. Uyvus. Econo 2 servicios de con Unives Diamokonia Diamokovia Stoth Monthume	
TRUE PLIOCENE.		byaas, 5 spectes. masonout, 5 sp. Liamas, raaackaaa. 1 aaggonas. 51004, meyeengu. Feddre (?) Ilytenidae. Mustelidae.	Refination of Anadons and home
MIQCENE. Under	LOUP FORK.	Protohippus, Hipparion. Mastodon, Ruinoceroses, Aphelops, 5 species. Condide., Felder, Rodents. Edeniates. Camels and Llamas, Procametus, Problebis. Orcodons, 3 genera. Decr., Biokomergy, Cosory, 20.	less rhinoceroses.
	DEEP RIVER.	Protokippus, Auchitherium. First Mastodons, Oreodons, Cyclopidius, Chukeotherium. Tylopoda.	Disappearance of Chalicotherium. Ext. of Creodonts, Ilyænodous.
Middle.	JOHN DAY.	Michippus. Two-horned Rhinoceros, Diceratherium, Peccaries. Oreodons, Rodents, Canidae, Felidae. Typopoda.	Extinction of Elotheres and Hyo-
Lower.	WHTE RIVER. PROTOCERAS. (Upper.) OREODON. (Middle.)	(?) Michippus. Artionyx. Appearance of tragulines, foldheres, Hyppolanus, pizs and pco- cartes, true ducgs, cuts, monikeys. <i>Environmentar. Coloban.</i> Mesohippus. Amynodon. Gintleoduerium, Accorditerium, Techtonienum, Myriobarvas, Mesohippus. Titauotherium, Oposaus, Yiyopola, Federatherium, Creodont, Hygenodon, Mesohippus. Titauotherium. Gocenus. Insectivores.	potention. Extinction of Anynodous. Extinction of Amynodous.
	TUTANOTHERIUM.		Extinction of Titanotheres.
EOCENE.	UINTA.	Ephihippus. Annynodom. 'litanothere, Diplacodon. First Orcodous, Protoreadon. First Tylo- poda, Leptotragulus. Tapirs. Hyracodons. Rodents. Creodonts, Mesonyx.	
Upper.	BRIDGER. WASHAKIE.	Pachynolophus. Appearance of Amynodous and horned Titanotheres. Paleosyops. Hyrachyus. Triplopus. Achenodon.	Extinction of Dinocerata, of some
	(Upper.) Bridger.	Pachynolophus. Appearance of Insectivora, Cheiroptera, Hyracodons, Unitatherium. Patheo- syops. Creodonts.	Extinction of Tillodontia.
	(albddle)	llyracotherium. Pataosyops. Divocerata. Coryphodon. Phenacodus.	Extinction of Coryphodontia and
Middle.	WIND FLVER. (Lower.) WAUSATCH.	lies	compyratella. Exumetion of Arctocyons.
-	Interval.	(Differentiation of modern clauved and hoofed placentals.)	
LOWCE.	PUERCO.	Phiodus, Neoplagianiar, Polymastodon. Ancient types of Ungulates, Carnivores and Insec- tivores: Amblypoda, CondyLarthra, Creodonta. Tæniodonta. Tultodontia. Lemurs.	Extinction of Multituberculates, (? Monotremes).
TIPPER CRETACTORS	Interval.	(Differentiation of ancient clarved and hoofed placentals.)	Disappearance of Marsupials.
	LARAMIE. Interval.	Philodus, Bolodontidue (Multituberceulates), Thiceodon, Trituberceulate Placentals and Mar- suplals, typical dentrition.	
MIDDLE JURASSIC.	Atlantosaurus. Interval.	Clemeodon. Plaqiautar, Bolodon, Multituberculates (? Monotremes). Triconodonts (? Mar- suptais). Trituberculates (? Placentals), primitive dentition.	
UPPER TRIASSIC.	Chatham Coal Beds.	Protodontu, Dromotherium, Microconodon, primitive Triconodonts (? Monotremes).	

THE SUCCESSION OF THE NORTH AMERICAN MAMMALIA.

the Cernavsian of France. The Multituberculates of the Laramie include the Plagiaulacidæ, represented by Ptilodus, the form with two premolars, and Meniscoëssus, with two premolars and crescentic tubercles. Meniscoëssus has a smaller fourth premolar, and is found to lead off to the huge plagiaulacid Polymastodon of the Puerco. The only other Multituberculates found are those related to Bolodon of the Jurassic and Chirox of the Puerco. The other mammals of the Laramie range from the mouse to the opossum in size; they have superior molars of the simple tritubercular type-the low cusped or bundont molar predominating in the upper jaw, and the tuberculo-sectorial in the lower. The dental formula is mostly the typical p. 4, m. 3. Yet, judging by the angular region of the jaws, we have here both Placentals and Marsupials. Some of the teeth remind us strongly of those in the Puerco; their determination, however, is very difficult, for the jaws and teeth are almost entirely isolated. From another exposure of the Laramie, Cope has recently found the remarkable type Thlaeodon-remarkable because it is a highly specialized trituberculate of typical dentition with a jaw which bears resemblance to that of the Multituberculates and of Ornitho-There is no placental angle nor strong marsupial rhynchus. This raises the supposition that Thlæodon may be inflection. one of the persistent trituberculate Monotremes which we are now looking for.

In the Puerco or basal Eocene, a very marked change occurs, for the American fauna loses some of its cosmopolitan character, the Multituberculates or monotremes die out and the marsupials are not found at all; in fact they do not reappear in North America until the Miocene.

## Ancient and Modern Placental Differentiation.

The Puerco is essentially an archaic fauna and is to be regarded as the climax of the first period of placental differentiation, a culmination of the first attempts of nature to establish insectivorous, carnivorous and herbivorous groups. These attempts began in the Cretaceous, and some of the types thus produced died out in the Puerco, some in the Wahsatch and Bridger; only a few flesh-eaters survived to the Miocene. It is most important to grasp clearly the idea of this functional radiation in all directions of this old Puerco fauna, resulting in forms like the modern insectivores, rodents, bears, dogs and cats, monkeys, sloths, bunodont and selenodont ungulates, and lophodont ungulates. This was an independent radiation of placentals, like the Australian radiation of marsupials. What was the cause of the wide-spread extinction of these types? So far as the ancient clawed types are concerned, their teeth and feet seem to be as fully adaptive in many cases as those of the later unguiculates; the hoofed types were certainly inferior in tooth evolution, for all their molars evolved on the triangular basis instead of the sexitubercular; the most sweeping defect of both the clawed and hoofed types, was the apparent incapacity for brain growth, their bodies went on developing while their brains stood still. Thus the stupid giant fauna, the Dinocerata, which rose out of this period, gave way to the small but large-brained modern types. It is noteworthy that the latest survivors of this wreck of ancient life were the largebrained Hyænodons.

Some of the least specialized spurs of this radiation appear to have survived and become the centers of the second or mid-Tertiary radiation from which our modern fauna has evolved. Yet we have not in a single case succeeded in tracing the direct connection. To sum up, we find on the North American continent evidence of the rise and decline and disappearance of monotremes and marsupials, and two great periods of placental radiation, the *ancient radiation* beginning in the Mesozoic, reaching a climax in the Puerco and unknown post-Puerco, and sending its spurs into the higher Tertiary, and the *modern radiation* reaching its climax in the Miocene, and sending down to us our existing types.

Another Eocene center was lower South America, which has of late dimmed the prestige of North America in yielding strange forms of life. One theory of this Patagonian fauna is that it was an independent center of functional radiation like the Puerco and Australian, full of adaptive parallels, but not yielding to Europe or America any of their older types. But Ameghino, to whose energetic researches we are chiefly indebted, believes that he finds a lower Eocene life zone-a sort of south polar center—which supplied both America and The Puerco he believes is no older than the Santa-Europe. cruzian which in turn is very much older than the Parana and Pampean formations, which Burmeister has made so well known. This yields the Homunculus patagonicus which parallels Cope's Anaptomorphus in presenting a dentition as advanced in reduction as that of man. Ameghino finds here the ancestors of the Macrauchenidæ; he believes the Homolodontotheridæ are the ancestors of the Chalicotheriidæ-thus mistakenly deriving a buno-selenodont from a lophodont type; the Proterotheriidæ, he believes, replace the Condylarthra and

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Hyracotherium in the ancestry of the horses. Similarly the Microbiotheriidæ are the stem of the creodonts and carnivores. I cannot coincide with any of these views. The Multituberculates are far older and widely different from the Abderites to which Ameghino traces their ancestry. I fully concur with the opinion of Cope, Zittel, Scott and others that this fauna is of somewhat later age, that it was directly connected with Australia and somewhat later with North America, supplying us, as has always been supposed, with our sloths. I quote from a recent address by Scott:

"The oldest mammals from South America are those from Patagonia, which Ameghino has referred to the Eocene, but which are more probably Oligocene or Miocene. This fauna is of extreme peculiarity and isolation; it is made up chiefly of edentates, rodents and ungulates of those very aberrant types known as Litopterna and Toxodontia, which are so widely different from the hoofed mammals of the northern hemisphere; together with some primitive forms of primates, creodonts and marsupials. The marsupials are of extraordinary interest, for they comprise not only forms allied to the opossums, but also to recent Australian forms such as Thylacinus, Dasyurus and Hypsiprymnus. This is a most unexpected fact and seems to point unmistakably to a great southern circumpolar continent."

The North American Puerco thus remains the most extensively known and productive lower Eocene center yet we have very slender threads of positive evidence to connect its fauna with the later placental radiation.

The Creodonts of Cope occupy the same relation to the modern insectivores and carnivores that the Condylarthra do to the ungulates. The American group has been recently enriched by the discoveries of Wortman, and the literature by the careful revision of Scott. This author has divided them into eight families, placing the forms which most resemble the Insectivora in the new family, Oxyclænidæ. These families illustrate superbly the same law of functional radiation later repeated in the placental and marsupial carnivores. The Mesonyx family presents some analogies to the Thylacines. The modern bears are paralleled in the Arctocyons, with their low tubercular molars; Wortman and myself, with fresh materials, have recently added Anacodon to this family, a genus which was doubtfully regarded by Cope as an ancient ungulate. The Cats and Hyænas are imitated in the Oxyænas and Hyænodons, some of the Miocene forms of which Scott suggests developed aquatic habits; as above noted, some of this family acquired large brains and persisted well into the Miocene. A

still more remarkable likeness to the Cats is exhibited in the Palæonictis family, which, unlike the Hyænodons, forms its sectorials out of exactly the same teeth as the true cats. The first American Palæonictis was found two years ago by Wortman, and this author and myself have suggested that this may be the long-sought ancestor of the Felidæ. The Civets are anticipated in the Proviverridæ; yet both Cope and Scott, the highest authorities on this subject, believe that the dog-like Miacidæ alone formed the connecting link between the Creodonta and the true Carnivora.

The foot structure of the ancient Puerco ungulates is still only partly known. Cope has divided these animals into the Amblypoda and Condylarthra. The Amblypoda are represented in the Puerco by a large form called Pantolambda, with selenodont triangular upper molars, and possibly by Periptychus, with bunodont triangular molars. The Pantolambda molars were, as Cope has shown, converted into those of Coryphodon, the great lophodont Amblypod of the Wahsatch, by a process exactly analogous to that in which the anterior half of a Palæotherium molar was formed, that is, they acquired outer and anterior crests but no posterior crests. This Coryphodon molar type was still later converted into the Uintatherium type by swinging around the onter crest into a transverse crest. I have recently made a careful study of the fore and hind feet of Coryphodon, and have found that while the fore foot was subdigitigrade like that of the elephant, the hind foot was fully plantigrade, the entire sole resting upon the ground. The relation or connection between the Bridger Dinocerata and these earlier Amblypoda is still unknown. The Puerco Periptychus left no descendants. The other ungulates of the Puerco were the Condylarthra, including the primitive Phenacodontidæ, the supposed ancestors of the Artiodactyls and Perissodactyls. Much remains to be done to clear up their relationships.

#### Succession of the Perissodactyls.

In the Wahsatch and Wind River we find not only the last of the Phenacodonts and Coryphodonts and the first of the Dinocerata, but the first of the true Artiodactyls and Perissodactyls. Recent studies of Cope, Schlosser, Pavlow, Filhol have been directed to the phylogeny of the Perissodactyls with very different conclusions. I agree most closely with Schlosser, and have endeavored to show that the molar teeth give us a key to their natural arrangement as shown in this column.  $\ldots$   $\langle$  Titanotheres. ( Horses. 7 Palæotheres. Tapirs. Lophiodonts. (Helaletes). ( Hyracodonts. Amynodonts. Rhinoceroses.

Upon one side the Titanotheres present the buno-selenodont extreme with most analogies to the Artiodactyla in tooth structure and in their truly Artiodactyl fore feet and bony horns. (If, as Cope supposes, the Diplarthra form a natural group, some Perissodactyls should certainly be more Artiodactyl than others.) The

Horses and Palæotheres diverge from the buno-selenodont type towards the Lophodont; they were early separated in foot structure. The Tapirs, Lophiodonts, and Helaletes show wellmarked transverse crests and incipient external crests. This brings us to the other Lophodont extreme, the Rhinoceros-like forms, with complete transverse and external crests. There are many other minor characters which support this as the natural arrangement of the Perissodactyls. I think it can be shown conclusively that these eight or nine series diverged from each other before the Wahsatch, and that all attempts to derive them from each other in later periods will break down. They will be found to converge into the unknown Sub-Wahsatch period, to stem forms as indicated by the brackets.

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The Titanotheres have been traced by Cope back to Lambdotherium in the Wahsatch; in the Wind River the true Palæosyops is found, and in the Bridger this becomes the predominant perissodactyl family, and spreads out into a great variety of forms, which have recently been carefully described by Earle. In the Washakie there are some still larger forms, and Marsh has traced the line through the teeth of Diplacodon of the Uinta to the true Titanotheres. Still the origin of the flattened skull and remarkable anterior pair of horns has never been known; Hatcher reports species with very small horns in the base of the Titanotherium beds (Lower Miocene). Wortman has just reported to me the brilliant discovery of an upper Eocene (Bridger and Washakie) Palæosyops with a flattened skull and rudimentary horns just appearing upon the nasals! This forms the desired connecting link.

The early history of the horses, probably starting with the Puerco Condylarth Euprotogonia, and passing through Hyracotherium, Pachynolophus, Epihippus, Mesohippus, is now familiar enough. It is the later history which requires elucidation, and is producing the most unexpected number of parallel lines of horses, out of one of which only our modern horse sprang. Here we are especially indebted to Cope, Pavlow, By general consent Hipparion comes out of its and Scott. old position in the true line as displaying the most extreme variations in the crowns of the molar teeth in compensation for the backward evolution of its feet. Scott has been especially investigating the upper Miocene horses; I quote from the MSS. he has kindly lent me, in which he proposes to remove also the classical Anchitherium of Cuvier. He says: "These American genera, Mesohippus and Miohippus may confidently be regarded as important members of the equine stem, while Anchitherium (of Europe) from present information would appear to belong to an abortive side branch leading to no permanent results." Scott has also discovered an important intermediate form linking Miohippus with Protohippus.

The Palæotheres have not been found in America.

The Tapir line has been traced by Cope and myself back to Systemodon of the Wahsatch, and Isectolophus of the Bridger and Uinta. These forms have simple premolars, but bear the most striking resemblance to the Tapirs in the molars both above and below. All previous attempts to determine the Miocene representatives of the Tapirs have been erroneous. Wortman and Earle have just published an account of two lower Miocene species of true Tapirs, which, both in foot and tooth structure, definitely carry the American Tapir line up to the middle Miocene, where it is again lost sight of. These species belong to the genus Protapirus, which Filhol has found in the Oligocene of France, thus adding an important geological parallel. The Wahsatch Tapirs were a little larger than the Horses or Hyracotheres which were about the size of a fox, and much smaller than the ancestral Titanotheres.

Another family of small, slender perissodactyls more nearly allied to the Lophiodons of Europe than any other American forms are the Helaletidæ, distinguished by feet tending to monodactylism, and narrow hoofs like those of the deer; even in the Wahsatch Heptodon the lateral toes are quite short and raised off the ground. The molars, like those of the lophiodons of Europe, are intermediate between those of the Tapir and the Rhinoceros, but both teeth and feet preclude our uniting these forms either with the Tapirs or with the Hyrachyus family, as Cope has done. The Bridger successor is Helaletes, which Marsh mistakenly supposed was an ancestral Tapir, and the integrity of this line is now firmly established by the discovery of the Miocene Colodon. This is described by Marsh as a successor of Helaletes, and Wortman and Earle have just published an account of the teeth and feet, showing that Colodon is widely separated from the contemporary true Tapirs, and is the last member of the Heptodon-Helaletes line.

The Rhinoceroses of America comprised the true Aceratheriinæ and Diceratheriinæ, and what may be called the

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pseudo-rhinoceroses, the Hyracodons and Amynodons; all these forms present the true Rhinoceros molar pattern, but they diverge most widely in the structure of the anterior teeth and of the feet. The Hyracodons first appear in the numerous and diversified Hyrachyus of the Bridger, some of which exhibited rudimentary horns upon the back part of the nasals (Colonoceras); they retained a full set of equal-sized incisors and canines, and acquired a horse type of skull, skeleton, and locomotion. Scott has well named them the "cursorial rhinoceroses." Colonoceras probably did not, as Marsh has suggested, branch off into Diceratherium, for the horns of this true rhinoceros are developed at the ends of the nasals; the Hyrachyinæ sent off as a side branch the deer-like Triplopus of the Washakie, and terminated in the Hyracodons of the lower Miocene.

The Amynodons, at the time of their discovery by Marsh, were naturally supposed to be the long-sought Eocene rhinoceroses, but I have shown that no Amynodon can fill this rôle. Garman's discovery of the skull of the remarkable Miocene Metamynodon tended to confirm my views, and I have now to report the discovery of many skulls and a nearly complete skeleton by the American Museum Expedition. This proves that the Amynodontidæ were remarkable side forms. In wide contrast with the true rhinoceroses, the upper and lower canines develop into huge, partly recurved tusks, like those of the boar. As in Elasmotherium, the premolars become greatly reduced, and the molars tend to hypsodontism. The lower molars are long and narrow, like those of the anomalous Cadurcotherium of the Oligocene of Europe-it is thus rendered probable that Cadurcotherium is not a sloth, as Filhol has suggested, but is an aberrant rhinoceros, related to, if not identical with, the Amynodons. The hypsodontism in some Metamynodon teeth is accompanied by a partial loss of enamel. To complete the aberrant character of this family, we find that it has four equal-sized and completely functional toes in the forefoot, like those of the Titanotheres, not with the fifth toe reduced as in the contemporary Aceratheria.

The true Rhinoceroses, we remember, are distinguished by the entire loss of upper canines. Wortman has just reported finding rudimentary upper canines in both the milk and permanent dentitions of the older Miocene species. The true rhinoceroses suddenly appear in the lower Miocene of America and Oligocene of Europe; we have not yet traced them back. In a collection of lower Miocene skulls recently obtained for the American Museum we find that the premolars are still very simple. In the higher Oreodon beds all traces of the superior canine are lost, and the premolars have become more like the molars. As the origin of the rhinoceroses still remains a mystery, so their later evolution needs clearing up. The American series suddenly terminate in the huge, hornless forms of the upper Miocene. I find there is still no unanimity of opinion as to the phyletic relationships of the Miocene, Pliocene and existing species of Europe.

#### Succession of the Artiodactyls.

The Eocene Artiodactyl phylogeny is still far behind that of the perissodactyls, but the Miocene and Pliocene succession has been worked up with great success and clearness by Cope and Scott. The latter says in a recent paper: "All the great groups of Artiodactyla are seen to arise independently from the Buno-Selenodonta which forms as it were a lake, from which several streams, flowing partly in parallel partly in divergent directions, are derived."

The Elotheriidæ appear in Parahyus of the Bridger and Achænodon of the Washakie, and terminate in the middle Miocene in the gigantic *Elotherium ramosum*, an animal with a skull three feet long, both the jaws and skull being armed with long branching processes. The true bundont pigs and peccaries have not yet been found lower than the White River.

Scott has traced the Oreodons back to Protoreodon of the top of the Eocene. The aberrant Agriochæridæ, he believes, were doubtfully connected with the true Oreodons by a lower Eocene stem form. The true Oreodons, which existed in great herds in the lower Miocene, have been divided by Cope and Scott into three parallel lines extending into the Loup Fork, namely, the large Merycochærus, the medium-sized Merychyus and the small, highly-specialized Pithecistes.

The Tragulines are represented by Leptomeryx, Hypertragulus and Hypisodus. Leptomeryx is believed to be a side member of the main family.

Here I may speak of the recent discovery of the characters of the Protoceratidæ, a new family with a remarkable ensemble of characters. In 1891 Marsh described the female skull of Protoceras with a small pair of parietal protuberances. The male skull was found by the American Museum party of 1892. It is armed not only by upper canine tusks, but by four pairs of cranial protuberances, two of which might be dignified by the name of osseous horns; it thus presents the armature of an Uintatherium upon a small scale. Besides parietal and two pairs of frontal protuberances, there are a pair of most exceptional maxillary plates. The fore foot is like that of Tragulus, while the hind foot is didactyl like the deer. We can at present form no idea of its affinities.

The oldest American Artiodactyl certainly known is the tritubercular Pantolestes of the Wahsatch. Cope believes the line of American Llamas may have sprung from this, and have been continued through Homacodon of the Bridger. The first undoubted cameloid is Leptotragulus of the Uinta, a comparatively recent discovery. It has strikingly reduced feet for such an early form. Pœbrotherium of the White River and John Day has quite the proportions of the living llama; thence the line passes into Protolabis of the Deep River and John Day. Scott believes that these forms are undoubtedly related to both the camels and llamas, and that in the Loup Fork, perhaps in the two species of Procamelus, the division occurs, P. angustidens passing into the camels, and P. occidentalis into the llamas. The Pliocene Homocamelus, Holomeniscus and Eschatius, Scott believes may represent a highly specialized side line of camels; while Pliauchenia, still imperfectly known, may belong on the llama side.

The deer represented by Cosoryx and Blastomeryx are, so far as we know, not of American origin, for they first appear in the Upper Miocene at Loup Fork.

### The Ancylopoda.

The order Ancylopoda Cope presents the most signal exception to the law of correlation. It is only quite recently that Filhol, Forsyth Major and Depéret have brought together the sloth like phalanges with the ungulate type of teeth of the Chalicotheriidæ. Since 1825, when Cuvier described the phalanges from Eppelsheim as those of a "pangolin gigantesque," referring to their deep clefts, and 1833, when Kaup named the teeth, these structures were always considered distinct. It is probable that Moropus and other supposed Sloths described by Marsh from our Miocene also belong in this exceptional order. As now restored by Filhol and myself, this remarkable Chalicotherium had a gait less clumsy than the Sloth, and something between a huge cat and a hoofed animal; it combined the skull of a primitive ungulate with the molars of an eocene titanothere, for the premolars are simple. The limbs, wrist and ankle bones are chiefly ungulate and perissodactyl. In viewing this combination of characters, the first question to settle is which set of characters is secondary and adaptive. I agree with Depéret, as against Filhol who regards this as an aberrant edentate, that the unguiculate characters are secondary; but I do not believe it is very near the Perissodactyla. It seems to have sprung rather from the primitive ungulate stem before it had parted with its unguiculate characters. Perhaps it came off from the Wahsatch

Meniscotherium, a member of the Condylarthra, which it very closely resembles in its skull and molar structure and in its dental curve. Marsh, by the way, has just added to our knowledge of this little Wabsatch genus by describing its fore and hind feet, which are more primitive than those of Phenacodus or Hyrax. While the Creodonta were imitating all modern carnivores, is it not possible that the Condylarthra gave off a sloth-like form for fossorial and semi-arboreal habits?

Last summer while this problem was being discussed, we were brought face to face with the exact counterpart of Chalicotherium which may be called a *clawed odd-toed* form, by the surprising discovery of a hind foot, which represents a *clawed* even-toed animal. This was found by the American Museum party in the Protoceras beds of South Dakota, and has been named Artionyx. This foot has a truly Artiodactyl tarsus and metatarsus like that of the pigs or oreodons. Yet it possesses five toes terminating in large uncleft claws. It has been suggested by Wortman and myself that it represents an Artionychine (even-clawed) division and that Chalicotherium represents a Perissonychine (odd-clawed) division of the Ancylopoda: in other words, that a double parallelism exists with the Ungulata. Another explanation may be that these genera are highly specialized Artiodactyla and Perissodactyla respectively; Scott has made the ingenious suggestion, tending to support this theory, that the Artionyx foot is the long unknown foot of the aberrant oreodont Agriochærus of Leidy. This summer will probably determine the truth of this suggestion, for two parties are hunting in the beds in which Agriochœrus and Artionyx occur.

Thus an immense number of problems still await solution, and demand the generous coöperation of European and American specialists in the use of similar methods of research, in the prompt publication of descriptions and figures, and in the free use of museum collections. I may be pardoned for calling general attention to the service which the palæontological department of the American Museum is trying to render in the immediate publication of stratigraphical and descriptive tables of western horizons and localities.

### The Factors of Evolution.

A few words in conclusion upon the impressions which a study of the rise of the mammalia gives as to the factors of organic evolution. I refer also to recent papers by Cope, Scott and myself.

The evolution of a family like the Titanotheres presents an uninterrupted march in one direction. While apparently

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prosperous and attaining a great size, it was really passing into a great corral of inadaptation to the grasses which were introduced in the middle Miocene. So with other families and lesser lines, extinction came in at the end of a term of development and high specialization. With other families no causes for extinction can be assigned, as in the lopping off of the smaller Miocene perissodactyls. The point is that a certain trend of development is taken leading to an adaptive or inadaptive final issue—but extinction or survival of the fittest seems to exert little influence *en route*.

The changes *en route* lead us to believe either in predestination—a kind of internal perfecting tendency, or in kinetogenesis. For the trend of evolution is not the happy resultant of many trials, but is heralded in structures of the same form all the world over and in age after age, by similar minute changes advancing irresistibly from inutility to utility. It is an absolutely definite and lawful progression. The infinite number of contemporary developing degenerating and stationary characters preclude the possibility of fortuity. There is some law introducing and regulating each of these variations, as in the variations of individual growth.

The limits of variation seem to lie partly in what I have called the "potential of evolution." As the oösperm or fertilized ovum is the potential adult, so the Eocene molar is the potential Miocene molar. We have seen that the variations of the horse and rhinoceros molars, apparently so diverse, are really uniform,—is not this evidence that the stem perissodactyl had these variations *in potential*, waiting to be called forth by certain stimuli? This capacity of similar development under similar stimuli is part of the law of mammalian evolution, but this does not decide the crucial point whether the stimulus is spontaneous in the germ or inherited from the parent. I incline to the latter opinion.

Columbia College, August 3, 1893.

# ART. LXII.—On the Thoracic Legs of Triarthrus; by C. E. BEECHER.\*

THE first conclusive evidence of the presence of legs and gills in the Trilobita was given in 1876 by C. D. Walcott,+ who by means of translucent sections was enabled to demonstrate their existence in four genera, and to indicate several important points in their structure. The genera shown to possess legs were Ceraurus, Calymene, Asaphus, and Acidaspis. Various announcements of the discovery of the legs of trilobites had been made previously, but, with the exception of a specimen described by Billings in 1870, these proved to be erroneous determinations. Walcott has since made further studies, and brought together his conclusions in a paper published in 1881.<sup>‡</sup> Until 1893, no additions of note have been made beyond those confirming the fact that these animals possessed jointed legs. The specimens investigated by Walcott consisted chiefly of coiled individuals in which the body cavity was filled with calcite and clayey matter. There was no actual mineralization of the appendages, but the fillings of the cavities left by the decay of these organs served to show their general form. On account of their enrolled condition, considerable difficulty was experienced, and there was also a liability to error in attempting to determine the precise characters of the organs observed. Notwithstanding these drawbacks, some of the main points in the ventral anatomy of these animals were established.

The occurrence of Triarthrus Becki Green, in an exceptionally perfect state of preservation, from the Utica Slate near Rome, N. Y., has already been noticed in this Journal.§ In their present condition, the specimens contain very little calcareous matter, and nearly the entire calcareous and chitinous portions of the animal are represented by a thin film of iron pyrite. To this kind of fossilization is doubtless due the preservation of delicate organs and structures which otherwise would have been destroyed. For, as is well known, pyrite may replace such organic tissues as chitine or even soft dermal structures, the change occurring by the slow decomposition of

\* Abstract of a paper "On the Structure and Development of Trilobites' read before the National Academy of Sciences, November 8, 1893.

Preliminary Notice of the Discovery of the remains of natatory and branchial appendages of Trilobites. 28th Ann. Rept. N. Y. State Museum of Natural History, published in advance. December, 1876.
the Trilobite: new and old evidence relating to its organization. Bulletin of the Museum of Comparative Zoology, vol. viii, No. 10, 1881.
§ Vol. xlvi, pp. 121-125, 378-379, August and November, 1893.

these tissues in the presence of iron sulphate in solution, or from the action of hydrogen sulphide as a result of decomposition in a chalybeate water.

It was apparent that specimens preserving organs so delicate as antennæ ought to show in addition other anatomical features of great interest. This expectation has been fully realized in the study and preparation of the collection belonging to the Yale University Museum, but at present it is proposed to give only a preliminary description, and to figure some of the details of the thoracic legs.

No essential differences have been observed in the series of legs attached to the segments of the thorax. Each segment bears a pair of biramous appendages originating at the sides of the axis (Walcott). The anterior legs are the longest and the others gradually become shorter towards the pygidium. Those which are here taken for description are the legs of the second and third free thoracic segments. The entire length of the legs has been exposed, from the dorsal side, by removing the overlying pleuræ of the thorax which concealed nearly half their length. Each limb consists of two nearly equal members, one of which was evidently used for crawling and the other for swimming. These two members and their joints may be correlated with certain typical forms of Crustacean legs among the Schizopoda, Cumacea, and Decapoda, and may be described in the same terms. Therefore, each limb is composed of a stem, or shaft, with an outer branch (exopodite), and an inner branch (endopodite). Figure 3 shows the joints of the stem (6, 7), the exopodite (ex, 1 and 2), and the endopodite (en, 1-5). The precise details of the coxal joint of the stem (coxopodite) have not yet clearly been made out. It is followed by a broad joint about twice as long as wide, which may be referred to the protopodite.

The endopodite was the member used for crawling, as in the *Schizopoda*. The three proximal joints, the ischiopodite (5), meropodite (4), and carpopodite (3), are similar in form to the protopodite (6), and taper gradually outwards. The distal portion is completed by two shorter cylindrical joints, the propodite (2) and the dactylopodite (1), the latter bearing at its extremity short setæ, or bristles, of which three are commonly to be seen.

The other member, the exopodite, lies over the endopodite. It apparently articulates with the protopodite, but may spring from what is here referred to the coxopodite, as its basal portion is very broad and originates close to the articulation of protopodite with the coxal joint. The proximal joint of the exopodite (2) is somewhat arched and tapers rapidly. It extends to the ends of the pleuræ, and is the longest joint of either branch. The posterior edge is finely denticulate, and carries a row of long setæ. The distal portion (1) is multiarticulate, being composed of ten or more joints. In general form, it is slightly crescentic, with the margins thickened, the anterior one being strongly crenulated. Long setæ extend posteriorly from the crenulations on the dorsal side of the leg, making a conspicuous fringe along the distal half of the exopodite.

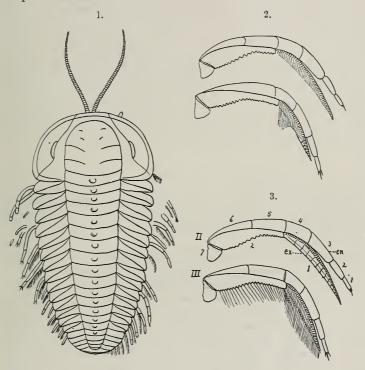


FIGURE 1.—*Triarthrus Becki* Green; dorsal view; showing antennæ and paired crawling and swimming thoracic legs  $\times 3$ . (The antennæ and legs on right side are from one specimen  $\times 3$ , and the legs of the right side are drawn from a smaller individual  $\times 6$ ).

FIGURE 2.—*Triarthrus Becki* Green; dorsal view of right legs of second and third free thoracic segments.  $\times 12$ .

FIGURE 3.—The same, with set omitted from II, to show details of structure ex, exopodite; en, endopodite. The set are represented on III. × 12

Figure 1 represents a dorsal view of *Triarthrus Becki*, showing the antennæ and the exposed portions of the appendages. The antennæ and legs on the right side are drawn from one specimen, and the legs on the left side are as shown in

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another individual. The biramous character of the entire series of thoracic legs is very evident, as is also the distinction between the crawling and swimming members. Figure 2 shows the right second and third legs of the free thoracic segments. In figure 3, the upper exopodite is represented without setæ, so as to bring out the structure in greater detail. On the lower leg the setæ are shown.

It is not proposed at this time to make any extensive comparisons or homologies with other groups of Crustacea, as the appendages of the head and pygidium still require further description and illustration, and will be the subject of a future contribution. It is evident, however, that the relations of the trilobites are with the *Entomostraca* and *Malacostraca*. Moreover, like the *Leptostraca* (*Nebalia*), the *Trilobita* probably constitute an intermediate type having affinities with the *Entomostraca* chiefly in the irregular segmentation, and with the lower forms of the *Malacostraca* (as the *Schizopoda*, *Cumacea*, and *Anisopoda*) in the detailed structure of the limbs.

ART. LXIII.—On the Diamond in the Cañon Diablo Meteoric Iron and on the hardness of Carborundum; by GEORGE FREDERICK KUNZ and OLIVER W. HUNTINGTON, Ph.D.

THE discovery of diamonds in the Cañon Diablo meteoric iron was first announced by Dr. A. E. Foote in this Journal for July, 1891 (vol. xlii, pp. 413-417). He found in the cutting of this meteorite that it was of extraordinary hardness, a day and a half of time being consumed and chisels destroyed in the process of removing a section. In cutting, the chisels had fortunately gone through a crevice filled with small cavities. The emery wheel used to polish this surface was ruined, and on examination the exposed cavities were found to contain hard particles which cut through polished corundum as easily as a knife cuts gypsum. The grains exposed were small and black, and Professor Geo. A. Koenig pronounced them diamonds because of their hardness and indifference to chemical agents. The extreme hardness was subsequently verified by one of us (G. F. Kunz), who carefully examined the type specimen.

On July 8, 1892 (Science, p. 15), Dr. Oliver Whipple Huntington gave the result of his experiments with this remarkably interesting Cañon Diablo iron. Taking one hundred grams of the iron he placed it in a perforated platinum cone suspended in a platinum bowl filled with acid, the cone being made the positive pole and the dish the negative pole of a Bunsen cell. The iron was slowly dissolved, leaving on the cone a large amount of black slime. This was carefully collected, digested over a steam bath for many hours, first with aqua regia, and afterwards strong hydrofluoric acid. A considerable part of the residue disappeared, but there remained a small amount of white grains which resisted the action of the acids. These particles, when carefully separated by hand, had the appearance of fine beach sand. Under the microscope they were found to be transparent and of brilliant luster. One of the grains was then mounted upon a point of metallic lead, which, when drawn across a watch crystal, was found to give the familiar singing noise characteristic of a glass cutter's tool and with the same result, namely, cutting the glass completely through. It deeply cut glass, topaz, and a polished sapphire. These facts, first announced in Science, April 8, 1892, were presented at the meeting of the American Academy of Arts and Sciences on May 11, 1892, and were published in the Proceedings of this Academy, new series vol. xxii, pages 252-253.

Later M. C. Friedel says in the Bulletin de la Société Francaise de Mineralogie,<sup>\*</sup> that he took a fragment of the Cañon Diablo meteorite weighing 34 grams, which gave the characteristic Widmannstattian figures, and treated it with hydrochloric acid. He digested the residue in aqua regia and obtained a black powder. After various treatments he thus separated about 35 gram of a powder which he presented to the Academy. The powder sank in a solution of the iodide of methyl having a density of 3.3. No grains measuring more than  $\cdot 5^{mm}$  to  $\cdot 8^{mm}$  were found, the powder being fine and impalpable, capable of scratching corundum. He also burned some of the black residue, and as a product obtained CO<sub>2</sub>.

At the meeting, above referred to. of the Academy of Arts and Sciences, Dr. Huntington showed to the members, under a microscope, the slightly vellow transparent grains he had obtained, and called attention to their adamantine luster. Not enough of the clear material was obtained at the time for a chemical test, and, on account of the association of the diamond grains with amorphous carbon, such a test would not have been conclusive without a perfect mechanical separation. One of us (G. F. Kunz) suggested that, if enough of the clear grains could be obtained to polish a diamond, it would conclusively prove that the material was diamond. For this purpose about 200 pounds of the meteoric iron was carefully examined, and specimens which appeared to contain diamonds were dissolved. The method used will be published by one of

<sup>\*</sup> No. 9, p. 258, Dec., 1892.

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us (O. W. Huntington) later. After enough material had been separated by Dr. Huntington, on Monday, September 11, 1893, through the courtesy of Messrs. Tiffany & Co., we were enabled to try the desired experiment in their diamond cutting pavilion in the Mining Building of the World's Columbian Exposition, they having prepared a new skaif or wheel, measuring  $10\frac{1}{2}$  inches in diameter, which was placed in position, the wheel having been specially planed down and prepared with the radiating scratches so as to be easily charged with diamond powder. A diamond was then soldered in a metal dopp and placed on the clean wheel, which made 2,500 revolutions to the minute. This diamond was tried for more than five minutes by itself without the slightest polish being produced, and no markings other than such as would be produced by the minute shattering of the diamond at extreme edges, due to the friction, as when a diamond is placed on an uncharged At 9:20 a cleavage, weighing five thirty-seconds wheel. of one carat was set with solder in the metal dopp which was placed on the wheel. The diameter of the wheel where the diamond was to be placed was four inches. The wheel was then charged with the residue from the meteorite (the powder mixed as usual with oil). The moment that the diamond was placed on the wheel a hissing noise was apparent, showing to an expert that the material was really cutting the diamond. At 9:23 a flat surface measuring 3mm by 1mm had been ground down and polished. At 9:30 a small crystal with a natural face up was set in the metal dopp, the crystal being a small natural complex twin weighing four thirty-seconds of one carat. It was first tried on a projecting angle. The cutting was very slow for a time, as the natural face of a diamond is always exceedingly hard. The position of the stone was then slightly changed, and a face measuring 2mm by 1mm was ground on the stone and cut. Three minutes later the surface had been cut down somewhat and a decided polish was produced on the triangular face, which was 3<sup>mm</sup> by 1.25. The fragment used was one of the octahedral faces of a crystal. The face ground down was at the angle of 45 degrees with the octahedral face. The entire time of this experiment was 15 minutes. The two experiments having been made with great care with both of us present, we cannot hesitate to pronounce the material diamond or a substance with the same hardness, color, luster and brilliancy.

In August last, one of us (G. F. Kunz) while examining the hardness of "carborundum," a carbide of silicon, made by Mr. Acheson of Pittsburg," it was found that it

\* See Engineering and Mining Journal.

readily scratched red, blue, white, pink, and yellow corundum in the form of fine gems. It having been suggested that this material would cut and polish a diamond, an experiment was made on a new wheel. After several trials had been made, it was found that carborundum would not scratch or polish the diamond, but on the other hand it was easily scratched by diamond cleavages, and crystal faces. This experiment is only mentioned as it precludes any possibility of the material which has been found in the Cañon Diablo meteorite being any such compound of carbon and silicon, such as the new and interesting abrasive material just mentioned. But it establishes the fact that we have an artificial substance that exceeds all natural substances except the diamond in hardness, i. e. being harder than 9—but still far distant from 10.

## SCIENTIFIC INTELLIGENCE.

# I. CHEMISTRY AND PHYSICS.

1. On the Mass-composition of Water.-The mass-composition of water has been determined with great care by DITTMAR and HENDERSON, the synthesis being accomplished by the action of hydrogen on copper oxide. A specially devised apparatus was employed for the purpose consisting of the reduction tube, with the necessary purifying and drying train before it and the water receptacle and drying tubes after it. About 115 grams copper oxide was placed in the reduction tube, and this was heated on a magnesia bath in a current of dry air. The next day the tube was exhausted, filled with hydrogen, allowed to assume the temperature of the balance case, again exhausted noting the pressure, and weighed. The apparatus was thus connected together, several liters of hydrogen were passed through it to free it of air, and the reduction tube was heated. The reduction of the copper oxide takes place below redness, the water receptacle being cooled first by ice and then by water. After the reduction is complete, the apparatus is allowed to cool, the hydrogen contained in it is replaced by dry air, and its various parts are dis-connected and weighed. The loss of weight of the tube gives the mass of oxygen employed and the increase of weight of the water flask and its drying tubes, the mass of water produced. The values obtained were carefully corrected. The first series of experiments was made to test the apparatus and to acquire familiarity with it. The results of the second series show that as a mean of the experiments 8 grams of oxygen required 1.00879 grams of hydrogen to form water; the result of the seven best experiments being 1.00848 grams. Hence they adopt as the

atomic mass of hydrogen 1.0085 (O = 16); or calling the atomic mass of hydrogen 1, the value 15.866, practically 15.87 as the atomic mass of oxygen. The atomic mass of hydrogen has been found by Stas to be 1.0075, by Cooke and Richards 1.0083, by Noyes 1.0072, by Lord Rayleigh 1.0069 and by Keiser 1.0032.— Chem. News, lxvii, 54, 68, 77, 90, 104, 115,126, 139, 151, 164, 1893.

2. On the Constitution of Hydrogen peroxide and of Ozone.-In 1886, TRAUBE expressed the opinion that hydrogen peroxide contains its oxygen atoms doubly united, so that this substance is a compound of an oxygen molecule with two hydrogen atoms,  $H_{a}$ , O = O. In support of this view he now brings forward certain significant facts. In the first place, no instance is known of the formation of hydrogen peroxide by the oxidation of water, the author's experiments showing that it is produced synthetically only by the action of molecular oxygen upon hydrogen. Thus it is formed at the kathode of the voltameter, where the evolved hydrogen meets gaseous oxygen. It is produced in processes of slow combustion, as in the case of zinc for example, where the hydrogen set free from the water comes in contact with oxygen gas. It is also generated by the combustion of hydrogen and also by the action of hydrogen palladium upon oxygen. In the second place, hydrogen peroxide exerts an oxidizing action only upon strongly reducing substances, being then rearranged into two hydroxyl groups which unite directly;  $Zn + H_2O_2 = Zn(OH)_2$ . That these hydroxyl groups do not preexist in the peroxide appears to the author to follow from the complete indifference which this substance shows compared with other oxidizing agents. Thus Schönbein found that it does not react at once upon either phosphorus or phosphorus acid. Welzien states that the titer of a peroxide solution did not change after standing over phosphorus for two months; and Schönbein observed that this substance could even be distilled with ether without decomposition. In alcohol, according to Lustig, the peroxide remains unaltered even in presence of sulphuric acid. In very dilute solution, it liberates iodine from potassium iodide only very slowly and potassium oxalate may be boiled with it without being oxidized. In further proof that hydrogen peroxide does not consist of two hydroxyl groups, the author notes the fact that, were this the case it should be obtained by the electrolysis of barium hydroxide; whereas no trace of it is produced in this process, only ordinary oxygen appearing at the anode. Ozone resembles hydrogen peroxide in many respects. If the constitution of the latter is H-O-O-H, that of the latter must be  $\frac{O-O}{O/}$ , its three atoms having the same chemical But if hydrogen peroxide is  $H_2 \cdot O = O$  and ozone value.  $O \cdot O = O$  the doubly united atoms will react differently from the third atom. This latter case appears to be the fact. Thus when ozone acts on sulphurous oxide  $SO_2 + O_3 = SO_3 + O_3$ . Moreover

ozone and hydrogen peroxide react thus:  $O_3 + H_2O_3 = H_2O + (O_2)_3$ ; whereas on the single bond theory  $O_3 + (H_2O_2)_3 = (H_2O)_3 + (O_2)_3$ would represent the reaction. In these cases only one atom of the oxygen appears to be active. So potassium tetroxide which is ordinarily written K-O-O-O-O-K, actually absorbs oxygen in spite of its large content of this substance, and reduces readily acid solutions of potassium permanganate. None of its oxygen atoms therefore are active, and on treatment with acid it decomposes into hydrogen peroxide and ordinary oxygen, indigo-sulphuric acid, if present in the solution, remaining unaffected. Hence the author writes its formula  $K \cdot O = O \cdot O = O \cdot K$ . Such substances as these, which are not active oxidizers, the author thinks should not be called peroxides. He has proposed the name "holoxides" for them, to indicate that the oxygen atoms are doubly united in them and exist as a molecule. While water is a compound of one atom of oxygen, hydrogen holoxide is a compound of one molecule of oxygen with two atoms of hydrogen. He suggests too that oxygen may be trivalent; and in that case would write the constitution of hydrogen holoxide H-O = O-H, of potassium holoxide K-O = O-O = O-K.-Ber. Berl. Chem.

Ges., xxvi, 1471, 1476, June, 1893. 3. On the formation of Ozone at high Temperatures.—The peculiar odor of the oxygen made from a mixture of potassium chlorate and manganese dioxide has long been recognized, and has generally been confounded with that of chlorine. Schönbein, Chevreul, Poggendorff and others mention chlorine as being evolved in this reaction and Marignac says he obtained 3 mgrms. of silver chloride from the oxygen evolved from 50 grams potassium chlorate. BRUNCK, reasoning that if the chlorate really gave off chlorine on heating, free alkali would be formed and should exist in the residue either as such or in the form of potassium manganate, has carefully examined this residue and finds it to be completely colorless and perfectly neutral. This fact, taken in connection with the property possessed by the odorous gas, even after washing with strong potash solution, of bluing paper moistened with potassium iodide and starch, led the author to assume that this gas must be ozone. Experiments made with ozonized oxygen showed that ozone may exist not only at the temperature of decomposition of potassium chlorate but even for a short time at a red heat; only 80 per cent of a gas thus prepared being destroyed by passing it through a combustion tube heated to 350°. The quantity passing did not materially diminish when the temperature of the tube reached a dull red. Comparative tests were made between oxygen evolved from the chlorate mixture and oxygen ozonized in a Siemens tube. Both samples set iodine free from neutral potassium iodide, oxidize alcohol to aldehyde, lose their properties when passed over manganese dioxide at ordinary temperatures, and are unchanged by washing with strong potash solution. Though these results establish the identity of the odorous gas with ozone, yet it differs in some particu-

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lars from the ordinary forms of this substance. Thus its odor is exactly that of chlorine, its permanence is greater at high temperatures, as is shown by the mode of its production, it does not act upon a mercury surface, and organic bodies such as caoutchouc, are far less readily attacked by it. Moreover, the author observed that while pure potassium chlorate yields perfectly pure oxygen, the slightest trace of any indifferent substance such as potassium chloride or even silica, causes the production of ozone. Hence the purest chlorate of commerce yields an oxygen containing ozone. A mixture of equal parts pure chlorate and manganese dioxide gave on heating a gas containing 0.3 per cent of ozone; and when the dioxide was increased to 25 times the mass of the chlorate, the ozone present amounted to 1.55 per cent. Investigation showed that this action was not produced by all oxides, and that oxides may be divided into three classes: (1) those which are indifferent, such as the oxides of iron, copper and zinc; (2) those which heated by themselves in an atmosphere free from oxygen to the temperature of decomposition, yield ozone, this ozone increasing in amount by heating them in a current of oxygen but is absent when the oxide is heated with chlorate, such as the oxides of silver and mercury and the peroxides of lead and probably barium; and (3) those which give ozone only when heated to the temperature of decomposition in presence of oxygen and which evolve ozone also when heated with potassium chlorate to a temperature considerably below the decomposition-point of this salt, such as cobalt oxide, manganese dioxide and nickel sesquioxide. The author notices the curious fact that the admixture of a small quantity of sodium carbonate with the chlorate and manganese dioxide entirely prevents the production of ozone, the sodium being left in the residue as peroxide.-Ber. Berl. Chem. Ges., xxvi, 1790, July, 1893. G. F. B.

4. On the Preparation and Properties of pure Nitrogen.-The preparation of pure nitrogen by various processes has been examined by THRELFALL. He finds that the method depending on the absorption of the oxygen from air by passing it over heated copper is a very objectionable one, since besides the mechanical difficulties of connecting the various tubes to one another at these high temperatures and of preventing their permeability to gases, the chemical difficulties are also serious. The preparation of the pure hydrogen or carbon monoxide for the reduction of the copper oxide is one of the greatest. Removal of the oxygen by passing air over heated phosphorus is also unsatisfactory. And the nitrogen obtained by heating ammonium dichromate, even when this salt was purified with the greatest care, contained nitrous compounds. The method finally adopted was the absorption of the oxygen from air by means of metallic copper and ammonia, the last traces of oxygen being removed by chromous chloride, prepared by Resoura's method and evaporated in an atmosphere of carbon dioxide under diminished pressure. All india-rubber was excluded from the apparatus, the joints were

hermetically sealed, the tops carefully ground and sealed with The substances employed were themselves carefully mercury. The nitrogen thus obtained when examined in a tube purified. furnished with external electrodes, gave a spectrum free from the lines of hydrogen or hydrocarbons. The observation of Thomson and Threlfall in 1887 that nitrogen suffers a diminution of volume on passing the electric discharge through it, the author confirms. But he finds that this effect is not due to a molecular condensation of the gas as originally supposed; but is owing to the production of a compound between the mercury of the gauge and the nitrogen, probably a nitride of mercury analogous to the trimercuramine of Plantamour. This compound appears as a brown film on the glass when the discharge passes through the nitrogen over mercury at about 8mm pressure; nearly the whole of the nitrogen being eventually converted into it. It decomposes at about 200° and re-forms on cooling.-Phil. Mag., V, xxxv, 1, Jan. 1893. G. F. B.

5. On the Preparation of Carbon under High Pressure.-A series of experiments has been made by MOISSAN upon the influence of pressure on the crystallization of carbon at high tempera-When carbon is dissolved in iron between 1100° and tures. 3000°, either graphite or a mixture of graphite and amorphous carbon separates at the ordinary pressure on cooling. If however, the cooling be effected under a high pressure the phenomena are quite different. To produce this pressure the mass of iron is heated up to 2000° or 3000° and the exterior is rapidly cooled by means of water; this exterior is thereby solidified and the still liquid interior, expanding as it solidifies produces an enormons pressure. Or, charcoal made from sugar is compressed in a soft iron cylinder closed with a screw plug, and the cylinder is plunged into a crucible containing melted iron. The crucible is withdrawn from the fire and placed in water until its exterior is at a dull red, after which it is cooled in the air. By these processes three forms of carbon are obtained, the proportion of each depending on the conditions of the cooling; which are (1) graphite, (2) thin contorted, maroon colored flakes, and (3) diamond. The diamond is obtained as grains of gray-black carbonado, of sp. gr. 3.0 to 3.5 and as transparent fragments, having a waxy luster and marked with striæ. Both these varieties leave a minute ash when burned. Silver also has the power of dissolving carbon. If this metal be heated to boiling in a crucible brasqued with charcoal and then rapidly cooled on the outside by plunging it into water, carbonado of sp. gr. from 2.5 to 3.5 is obtained in small plates.—C. R., cxvi, 218, Feb. 1893. G. F. B.

6. On the Properties of Diamonds.—In a subsequent paper MOISSAN has given the results of an investigation to determine the temperature at which diamonds begin to burn in oxygen, these temperatures being measured by means of a thermoelectric couple. As the temperature is slowly raised, the combustion takes place slowly and without the production of light, the only

evidence of it being the effect produced by the issuing gas on solution of baryta. At about 40° to 50° above this slow combustion temperature, the burning becomes rapid and a distinct flame is visible. The eight different specimens examined gave results as follows: yellowish-brown carbonado burned at 690° with flame; black carbonado at 710°-720° with flame; transparent Brazilian diamond at 760°-770° without a flame; cut diamond from the Cape, at 780°-790°, without a flame; Brazilian bort at 790° without a flame and at 840° with a flame; Cape bort at 790° without a flame and at S40° with a flame; very hard bort at 800° without and at 875° with a flame. The harder the diamond as a rule the higher its point of ignition. Heated in hydrogen to 1200° Cape diamonds do not lose weight, though they may lose their transparency and become lighter in color. At this temperature dry chlorine and dry hydrogen fluoride have no action on them. The vapor of sulphur attacks them only at 1000°; but with carbonado, carbon disulphide is produced at 960°. The vapor of sodium has no action at 600°. Iron at its fusing point attacks the diamond readily and graphite separates on cooling. When heated with alkali carbonates at a high temperature the diamond is rapidly dissolved with evolution of carbon monoxide but no hydrogen. Hence it cannot contain hydrocarbons.-C. R., cxvi, 460, March, 1893. G. F. B.

7. Oxygen in illuminating Gas.—While great attention is being paid to the problem of transmitting energy by means of electricity, the problems of accomplishing the same results by means of compressed air and by gas are not being overlooked. In the year 1890 Mr. Edward Tatham, of New South Wales, suggested the addition of considerable quantities of pure oxygen to warm heavy oil gas to produce a higher illuminating power. Dr. L. T. Thorne later in the same year gave the results of some preliminary experiments with such a gas-which were extremely favorable. Preparations are being made at Huddersfield to produce this enriched gas on a large scale. It has been found that the admixture of six per cent oxy-oil gas increases the illuminating power of the corporation gas by the equivalent of five and a half candles. A marked increase is also noticed in the stability of the gas under storage. The increased cost of production due to such enrichment will not exceed a third of a penny per thousand cubic feet. - Nature, Oct. 19, 1893. J. T.

8. Refractive indices of Liquid Nitrogen and Air.—Professors LIVEING and DEWAR have determined these constants by the method of MM. Terquem and Trannin. This consists in suspending in the liquid whose index is to be determined, two plates of glass with a thin layer of air between them and measuring the angle of incidence at which the chosen ray suffers total reflexion at the surface of the air. Professor Dewar found "that in a double glass vessel of any form, where the outer and inner vessels are separated by even narrow vacuous spaces, liquid oxygen can be kept for a great length of time open to the air. Such a liquid, filtered through ordinary filter paper to remove solid carbonic acid, remains quite tranquil and beautifully transparent of a pale blue tint." Liquid oxygen gave  $\mu$ =1·226. Liquid nitrogen at -190° C. and at atmospheric pressure gave for the D line  $\mu$ =1·2053. Liquid air gave for the D ray  $\mu$ =1·2062. When certain proportions of nitrogen had evaporated from the liquid air results were obtained as follows:  $\mu$ =1·215,  $\mu$ =1·218.—*Phil. Mag.*, October, 1893, pp. 328-331. J. T.

9. Rotation air Pump.—Sprengel's pump and Geissler's pump are the forms of pumps which are used for obtaining high vacua. F. SCHULZE BERGE has invented a new form which combines the possibility of obtaining a high vacuum with a speed which compares with that of a mechanical air pump. Vacua have been obtained by this pump which are beyond accurate measurement on McLeod's gauge. Several forms of the new pump are given by the author.—Ann. der Physik und Chemie, No. 10, 1893, p. 368– 376. J. T.

10. Waves in air.—A. RAPS has employed Jamin's interferential refractor to study the rarefaction and condensation of air while transmitting sound waves. One ray of light is led through air at rest and the other is passed through the air which is in movement. The two rays give interference fringes. These are received through a suitable slit on a revolving cylinder which is covered with photographic paper. The difference in the air paths thus produce vibrating fringes. A spot on a dark fringe and a spot on a bright fringe produce wave-shaped curves which represent the movements of the vibrating air column. In this way the author studies the movement of air in organ pipes and the movement of sound waves in open air. A large number of photographic plates accompany this article.—Ann. der Physik und Chemie, No. 10, 1893, pp. 194–220.

11. Standards of low Electrical Resistance.—At the late meeting of the British Association at Nottingham, Principal JONES described a method of determining small resistances which is based upon the Lorenz method of determining this ohm. The method . consists in rapidly rotating a copper disc whose center is on and whose rotating axis coincides with the axis of a coil. The same current is led through the coil and the resistance to be measured. The difference of potential between the center and circumference of the rotating disc is made to counterbalance that at the ends of the resistance to be measured. A series of experiments on a resistance of  $\frac{1}{2000}$  of an ohm was given and it showed that the variation from the mean of the extreme values was 1 in 12,000.

J. T.

12. Equipotential and magnetic force-lines.—E. VON LOMMEL returns to a discussion of his explanation of the Hall effect. He gives several plates of the distribution of magnetic filings upon plates of various forms through which powerful currents are led and compares these figures with representations of equipotential lines and magnetic lines on similar formed plates given by Quincke (Pogg. Ann. xcviii, p. 382, 1856). He concludes that the Hall effect is due to the shifting of the equipotential lines or surfaces due to the electric current in a strong magnetic field.—*Ann. der Physik und Chemie*, No. 10, 1893, p. 316. J. T.

13. Hand- und Hilfsbuch zur Ausfüshrung Physiko-chemischer Messungen, von W. OSTWALD, 1893, Leipzig (W. Engel-mann.)-In this handy little volume of three hundred pages Ostwald has condensed the results of his extended and very exceptional experience in the practical details of the conduction of research in physical chemistry. The chapters treating glass blowing, weighing and the determination of solubilities and of molecular weights contain many valuable suggestions about these ordinary manipulations of the laboratory. Those on the determinations of temperatures, pressures, densities, surface tensions, heat quantities and critical data, together with those on optical and electrical measurements have very especial' interest for the physical chemist, and they would be of great service in purely physical work. The descriptions and explanations are all admirably clear, the book is practically arranged and well printed, and it is accompanied by various separately printed tables which materially enhance its practical value. J. E. T.

## II. GEOLOGY AND MINERALOGY.

1. The origin of Crystalline Schists.—In an address before the Geological Section of the British Association, Mr. J. J. H. TEALL, combatted strongly the common idea that crystalline schists belong exclusively to the earliest periods of the earth's history. He expressed himself as follows:

"The crystalline schists certainly do not form a natural group. Some are undoubtedly plutonic igneous rocks showing original fluxion; others are igneous rocks which have been deformed by earth-stresses subsequent to consolidation; others, again, are sedimentary rocks metamorphosed by dynamic and thermal agencies, and more or less injected with 'molten mineral matter'; and lastly, some cannot be classified with certainty under any of these heads. So much being granted, it is obvious that we must deal with this petrographical complex by separating from it those rocks about the origin of which there can be no reasonable doubt. Until this separation has been effected, it is quite impossible to discuss with profit the question as to whether any portions of the primitive crust remain. In order to carry out this work it is necessary to establish some criterion by which the rocks of igneous may be separated from those of sedimentary origin. Such a criterion may, I think, be found, at any rate in many cases, by combining chemical with field evidence. If associated rocks possess the composition of grits, sandstones, shales, and limestones, and contain also traces of stratification, it seems perfectly justifiable to conclude that they must have been originally formed by processes of denudation and deposition. That we have such rocks in

the Alps and in the central Highlands of Scotland, to mention only two localities, will be admitted by all who are familiar with those regions. Again, if the associated rocks possess the composition of igneous products, it seems equally reasonable to conclude that they are of igneous origin. Such a series we find in the northwest of Scotland, in the Malvern Hills, and at the Lizard. In applying the test of chemical composition, it is very necessary to remember that it must be based not on a comparison of individual specimens, but of groups of specimens. A granite and an arkose, a granitic gneiss and a gneiss formed by the metamorphosis of a grit, may agree in chemical and even in mineralogical composition. The chemical test would therefore utterly fail if employed for the purpose of discriminating between these rocks. But when we introduce the principle of paragenesis it enables us in many cases to distinguish between them. The granitic gneiss will be associated with rocks having the composition of diorites, gabbros, and peridotites; the sedimentary gueiss with rocks answering to sandstones, shales, and limestones. Apply this test to the gneisses of Scotland, and I believe it will be found in many cases to furnish a solution of the problem."

".... The origin of gneisses and schists, in my opinion, is to be sought for in a combination of the thermal and dynamic agencies which may be reasonably supposed to operate in the deeper zones of the earth's crust. If this view be correct, it is not improbable that we may have crystalline schists and gneisses of post-Silurian age in the northwest of Europe formed during the Caledonian folding, others in central Europe of post-Devonian age due to the Hercynian folding, and yet others in southern Europe of post-Cretaceous age produced in connection with the Alpine folding. But if the existence of such schists should ultimately be established, it will still probably remain true that rocks of this character are in most cases of pre-Cambrian age. May not this be due to the fact, suggested by a consideration of the biological evidence, that the time covered by our fossiliferous records is but a small fraction of that during which the present physical conditions have remained practically constant?"-Nat. Science, Oct. 1893.

2. Ore Deposits of the United States; by Prof. J. F. KEMP. 8vo, pp. 302. New York, 1893 (The Scientific Pub. Co.).—The author after several preliminary chapters treating on classification, the mode and occurrence of ores as deposits and in mineral veius, then proceeds to the main body of the work. This takes up each of the metals in turn and describes concisely one occurrence typical of the method of classification. The similar occurrences in other localities are mentioned and a full list of the literature is given. Thus all the various methods of occurrence of each metal and its ores are shown. The volume is copiously illustrated with cuts and diagrams. The author has collected within brief compass a vast amount of useful information while the very full bibliography greatly enhances its value. The appearance of this work is opportune and it will be of great service to students in metallurgy, miners and in general to the public interested in mines and mining. No book of similar scope has appeared in this country since that of J. D. Whitney in 1855.

L. V. P.

3. Sach- und Orts-Verzeichniss zu den Mineralogischen und Geologischen Arbeiten von Gerhard vom Rath. Im Auftrage der Frau vom Rath bearbeitet von W. BRUHNS und K. BUSZ. 197 pp. Leipzig, 1893 (W. Engelmann).—The scientific career of Professor G. vom Rath was remarkable alike for the amount of mineralogical work which he accomplished as for the minute care and accuracy displayed through it all. His skill in solving the most intricate problems in crystallography and in presenting the results to the eye will always be a matter of admiration to those who study his papers. To all concerned with mineralogical literature the present complete index to his many papers will be most useful, forming as they do a very important part in the history of the science.

4. Mineralogisches Lexicon für das Kaiserthum Oesterreich von V. vonZepharovich. III Band, enthaltend die Nachträge aus den Jahren 1874–1891 und die General Register. Nach des Autors hinterlassenem Manuscripte bearbeitet von F. BECKE. 478 pp. Vienna, 1893 (F. Tempsky).—This volume is published by the Vienna Academy at the cost of the Zepharovich fund. It forms the conclusion to the author's well known work upon the Mineralogy of Austria and is edited from the manuscript left by him. An alphabetical list of localities referring to the three volumes occupies the last two hundred pages.

5. Handbuch der Mineralogie von Dr. C. HINTZE. Siebente Lieferung. pp. 961-1120. Leipzig (Veit and Co.).—The seventh part of this exhaustive work, recently issued, is devoted to the orthorhombic and monoclinic members of the Pyroxene group.

6. On the meteorite from Hamblen Co., Tennessee; by L. G. EAKINS (communicated).—In a paper upon the Hamblen Co. meteorite in this Journal for October, 1893, there occur some errors in figuring the formulas of the siliceous portions, to which Prof. S. L. Penfield has very kindly called my attention. This part of the paper was hastily written several months after the analytical work was done, and to this haste, caused by pressure of entirely different matters, these errors are due. As Prof. Penfield suggests, the soluble portion of the silicates, giving the ratios :  $RO: Al_{0}O_{1}: SiO_{2} = 506: 222: 760$ , can, by assuming the FeO and MgO to exist as olivine, be divided, approximately into olivine and a calcium-aluminum silicate like anorthite, both of which are soluble in hydrochloric acid. The insoluble portion reduces to,  $RO: Al_2O_3: SiO_2 = .670: .146: .844$ , which probably represents a mixture of pyroxene and enstatite; one or both being aluminous.

# III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. Letters of Asa Gray, edited by JANE LORING GRAY. 2 vols., 8vo. Boston and New York. 1893. (Houghton, Mifflin and Company) .- This collection of letters illustrates Dr. Gray's scientific career, and much of his home-life, from his first acquaintance with Dr. Torrey, about 1831, down to November 27, 1887, the last active day of his life. In respect to home-life, and among his friends, they reveal the genial, kind, sympathetic, christian gentleman, and in respect to his favorite science they show a constantly widening view, from the time when he began to notice the more interesting plants of Oneida county, onward through his study of the flora of North America and his contributions to general botany, through his broader studies of the relations of botany to other sciences, until, his interest undiminished, and his judgment clear, he suddenly rested from his labors. Many of the letters written from 1860 for the next score of years are to Mr. Darwin, or relate in some way to the investigations which Mr. Darwin was making, or the theories he was advancing, and would furnish good material for "The evolution of Darwinism," were such a chapter to be written. Other letters contain a history of the "Flora of North America," almost from its beginning in 1838, through the period when new plants were pouring in from the Rocky Mountain region and the Pacific States faster than they could be classified, down to the days, when having completed the "Gamopetaleæ" of the "Synoptical Flora," the aged botanist was revising the earlier orders, although with the confession that "I begin to doubt if I shall hold out to accomplish much more." The last letter of all contains his final dictum on nomenclature and the warning that "this business of determining rightful names is not so simple and mechanical as to younger botanists it seems to be, but is very full of pitfalls." The editing of these Letters has been done most carefully and judiciously; and those who knew the kind and many-sided naturalist will only wish that more of them had been printed. D. C. E.

2. National Academy of Sciences .- The following is a list of papers presented at the meeting of the National Academy, held in Albany, Nov. 7-9:

SAMUEL H. SCUDDER: American Palæozoic cockroaches.

SETH C. CHANDLER: Additional researches on the motion of the Earth's pole. C. A. WHITE: Biographical memoir of A. H. Worthen.C. B. COMSTOCK: Biographical memoir of W. P. Trowbridge.

JAMES HALL: The geological map of the State of New York. The Palæon-

GEORGE L. GOODALE: Certain Histological relations between the subalpine Plants of the White Hills and of the Labrador coast.

CHARLES S. HASTINGS: On a new form of telescopic objective, as applied to the twelve-inch equatorial of the Dudley Observatory.

CHARLES E. BEECHER: On the structure and development of Trilobites. ASAPH HALL: Double stars

CHARLES L. DOOLITTLE: Latitude determinations at the Sayre Observatory. JOSEPH A. LINTNER: Insect voices.

CHARLES H. PECK: Edible and poisonous Fungi.

EDWARD S. MORSE: A new process of printing in color. J. MCKEEN CATTELL and CHARLES S. DOLLEY: On Reaction-times and the velocity of the nervous impulse.

3. Annalen der Physik und Chemie, published in Leipzig since 1790 by Johann Ambrosius Barth (now Arthur Meiner).-This long honored periodical has now completed more than a century. It was begun by Gren in 1790, continued till 1824 by Gilbert, again till 1877 by Poggendorff and is now edited by Prof. G. Wiedemann. The first number of the 50th volume is devoted to the present editor, a biographical sketch of whom is given by Prof. Helmholtz; an excellent portrait forms the frontispiece.

Die Photographie: oder die Anfestigung von bildlichen Darstellungen auf künstlichen Wege. Lehr- u. Handbuch von praktischen und theoretischer Seite; bearbeitet und herausgegeben von Julius Krüger: zweite Auflage, gänzlich neu bearbeitet von Ph. C. J. Husnik, 494, 12mo. Wien, Pest, Leipzig (A. Hartleben).

## OBITUARY.

ARCANGELO SCACCHI, the veteran mineralogist of Naples, whose long continued labors on the mineralogy and geology of Monte Somma and Vesuvius, have given such rich results to science, died on the 11th of October.

HERMANN AUGUST HAGEN, the well known entomologist, and since 1870, Professor of Entomology at Harvard University, died on the 10th of November. He was born at Königsberg, Prussia, in 1817 and his scientific work for many years was done there. In 1867, at the invitation of Professor Agassiz, he came to this country to take a position in connection with the Cambridge Museum of Comparative Zoölogy. Among his many important contributions to science, the most extended is his Bibliotheca Entomologica, published in 1862.

DR. GEORGE W. COAKLEY, emeritus professor of mathematics and astronomy in the University of the City of New York, died at his home in Brooklyn on the 2d of August, in the seventyninth year of his age. He came to this country from the West Indies during his boyhood, and was graduated with honor from Rutgers College in New Jersey. After some years of work as a teacher of mathematics, first in New York State and afterward in Maryland, he was called to New York City about 1860, to assume the chair made vacant by the withdrawal of Professor Elias Loomis, who had just changed his residence from New York to New Haven. Professor Coakley continued his work here for thirty years. As a teacher he was indefatigable, patient, and skillful. In personal disposition he was too modest and retiring to secure for himself all the recognition that was due him. During the latter years of his life he published a number of papers on astronomical subjects, and his last work was a text-book on Calculus, which has not yet been published. During a protracted illness his interest in astronomical progress never flagged, and his clearest and best writing was done after disease had unfitted him for active work. W. Lec. s.

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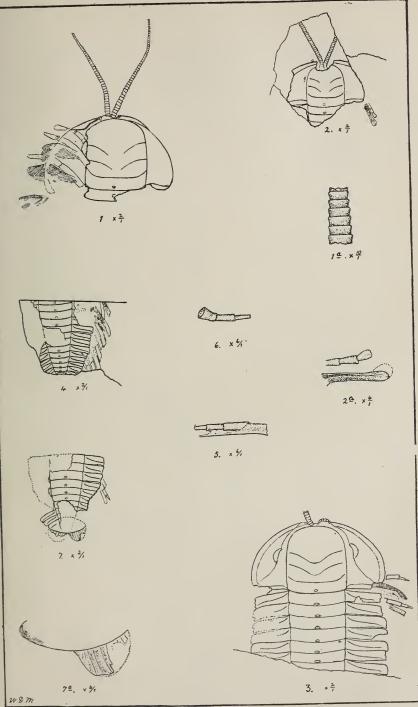
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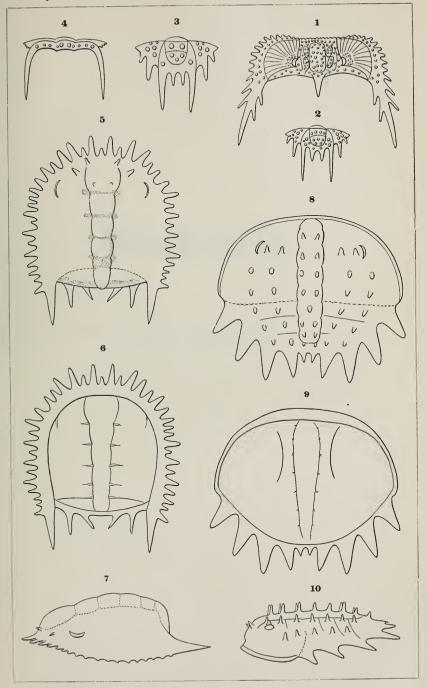
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ERRATUM.-On page 83 of this volume, last paragraph, for cathode read onode, for anode read cathode.



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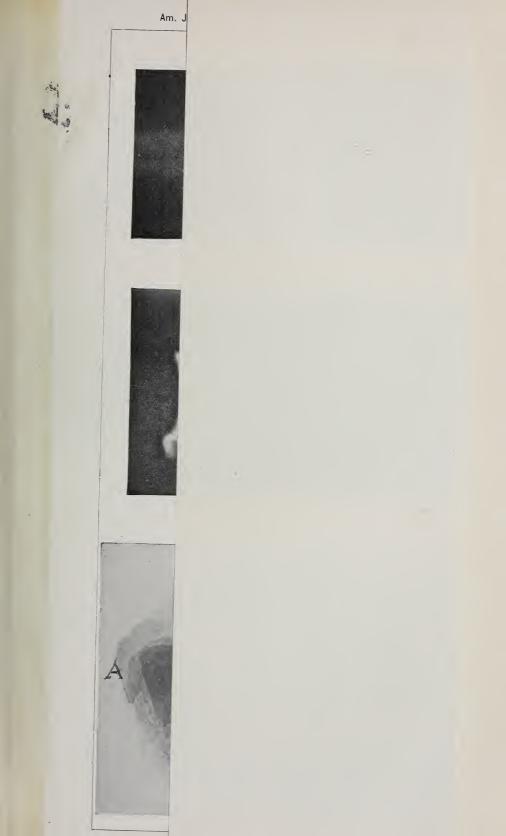
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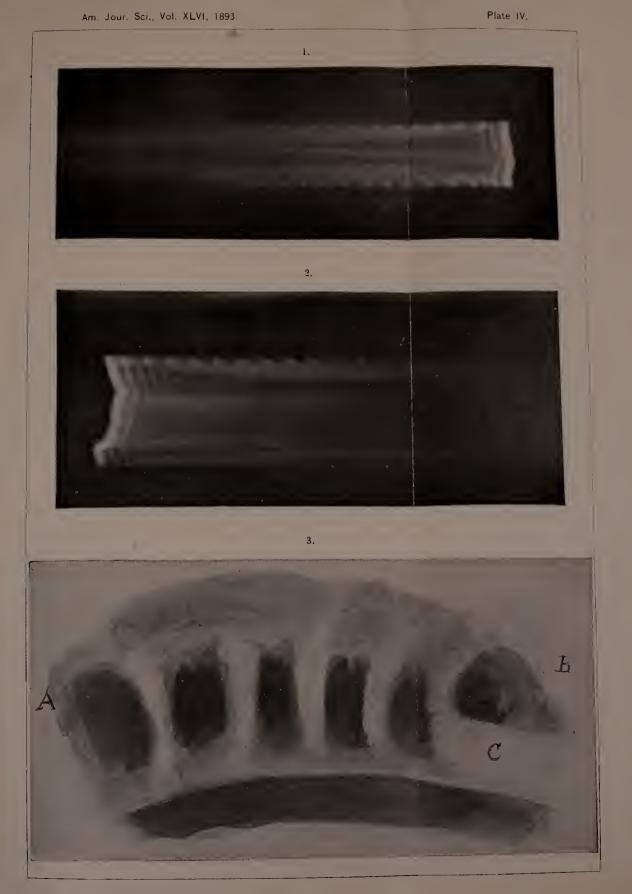
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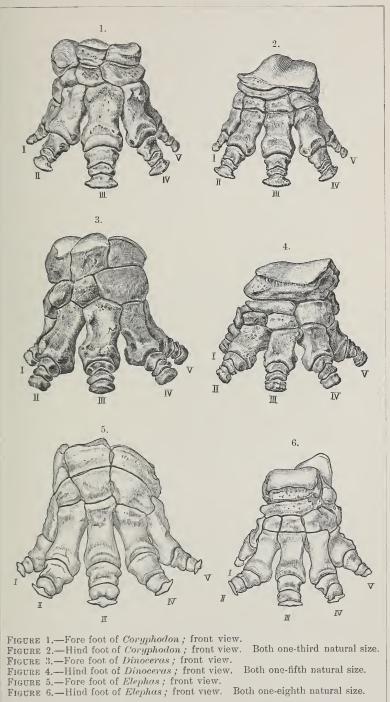


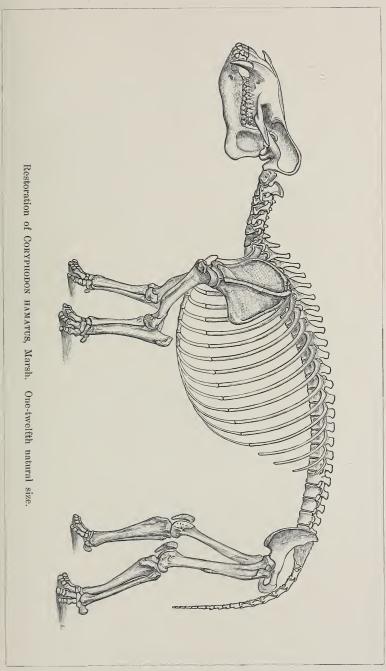


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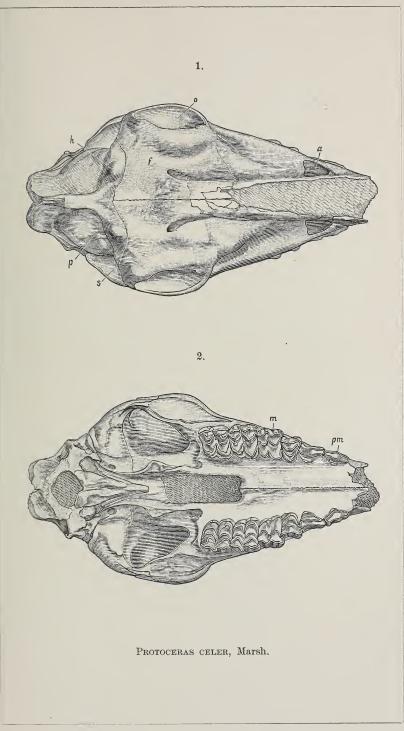
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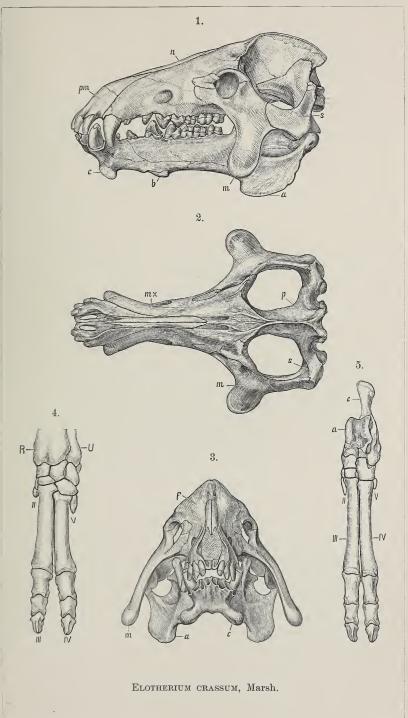


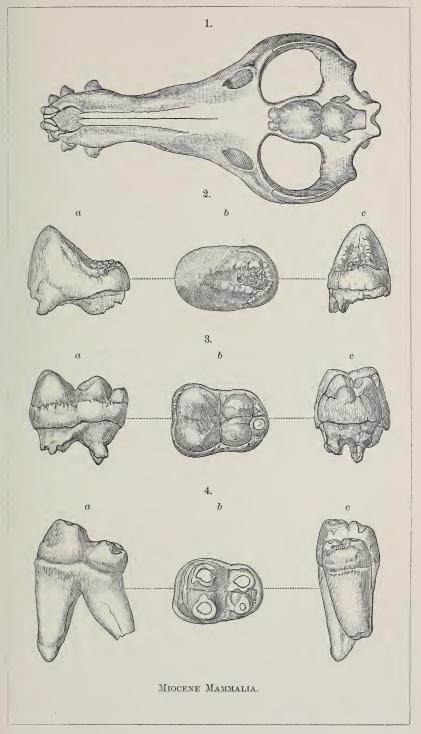


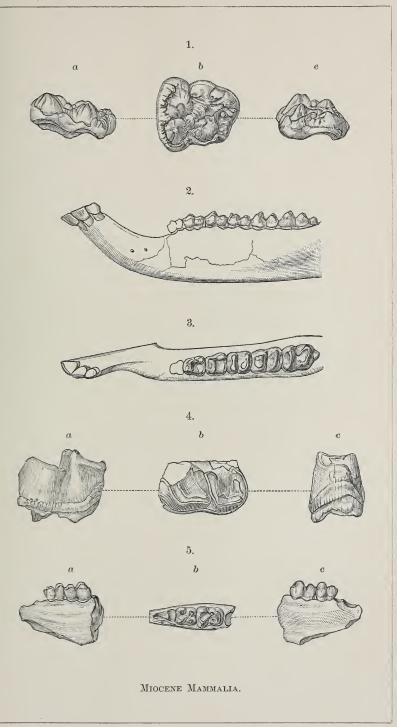
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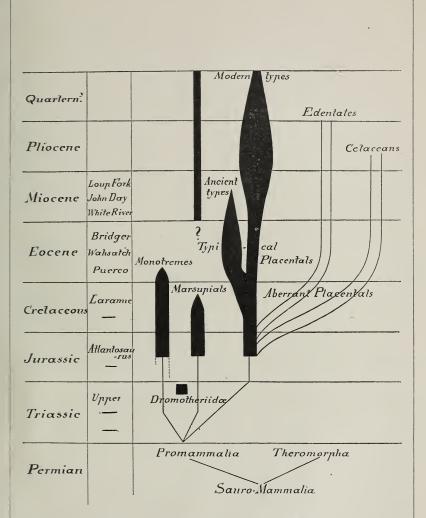








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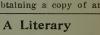
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